Freeze-Thaw Resistance and Microstructural Characteristics of Concretes Containing Pozzolans

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CERTIFICATE OF RESEARCH

This is to certify that, apart from where specific reference to other publications is made, the work presented in this thesis is the results of the investigations undertaken by the candidate.

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27.03.02 (Date)	27.03.02 (Date)	9/04/04 (Date)

DECLARATION

This is to certify that neither this thesis, nor any part of it, has been presented in candidature for any degree at any other academic institution

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G. Christodoulou
(Candidate)

DEDICATION

To
My Parents
and
in loving memory of my grandmother Kleopatra

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I always considered it over-fulsome of thesis authors to list a full list of people who were invaluable; always, that is, until I wrote a thesis and realized just how deeply I am in debt to the people below.

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ABSTRACT

The thesis describes a study undertaken to determine the effect of air entrainment on workability and air content of fresh concrete incorporating silica fume (SF), metakaolin (MK), fly ash (FA) and blends of FA and MK and to assess the effects of such pozzolans on freeze-thaw durability, air void system and microstructure of hardened concrete. Cement was partially replaced by various quantities of the pozzolanic materials. The results demonstrated that the increase in workability attributed to the air-entraining admixture was greater in MK concrete than in SF concrete and occurred for a greater range of dosages of the admixture. Improvements in workability due to the air-entraining admixture were also obtained in concretes with low levels (20%) of FA. Concretes with 30 and 40% FA although more workable, accrued no such benefit. In addition, the workability of FA-MK concrete was substantially reduced with increasing MK level at all total replacement levels, i.e. 20, 30 and 40%. Furthermore the air content tests indicated that up to 0.24% air entraining admixture resulted in steady increase in the air content of MK concrete, compared to a limit of 0.12% for SF concrete. Alternatively, FA caused large reductions in the air content of fresh concrete, irrespective of the dosage of the air-entraining agent. The freeze-thaw durability was determined on both air-entrained and non air-entrained concretes. Based on a criterion that unsatisfactory resistance to freezing and thawing corresponds to a durability factor (DF) less than 60% or a change in length greater than 200 μm/m, all the air-entrained concretes exhibited excellent performance under freeze-thaw conditions irrespective of the MK or FA content. On the other hand the non air-entrained concretes performed poorly under freezing and thawing. Thus, it would appear that air entrainment is the controlling factor for good freeze-thaw performance and the material effects are less important. However there were indications to suggest that non air-entrained concretes containing MK at low replacement levels (2.5 and 7.5%) could be frost resistant (DF > 80%). This was attributed to the increased spacing factor effected by the presence of fine particles of MK. Air entrainment was also a key factor for good scaling resistance. For instance, non air-entrained concretes with high replacement levels of MK (7.5 and 10% MK) exhibited more scaling than concretes with low replacement levels (2.5% MK), whereas scaling of air-entrained MK concretes was independent of the replacement level. The concrete containing high amounts of FA (30%) exhibited more scaling than the control and 10% FA concrete. However, blending FA with MK (MK/FA = 1/3) at total replacement levels of 10 and 30% improves the scaling resistance of the resulting concrete as compared to the FA only concrete. Non air-entrained concretes containing FA or blends of FA with MK showed an increase in weight at the beginning of freezing and thawing, an indication of uptake of water. Water absorption results confirmed that this was a result of a more open porosity. There is a strong correlation between sorptivity and pore refinement. Increasing amounts of the MK appear to cause refinemenent of the concrete's pore structure. As a result of this pore refinement sorptivity decreases with increasing amounts of MK. In addition blending FA with MK causes pore refinement. Irrespective of the pozzolanic material or blends of materials used the presence of entrained air appears to have a negative effect on pore refinement.

LIST OF CONTENTS

LIST OF ABBREVIATIONS

Pozzolans

SF	Silica Fume
FA	Fly Ash
MK	Metakaolin

Cement Chemistry

CH	Calcium Hydroxide
C-S-H	Calcium Silicate Hydrate gel

General

w/c	water to cement ratio
w/b	water to binder ratio
AEA	Air Entraining Agent
SP	Superplasticizer
HRWRA	High Range Water Reducing Admixture
PC	Portland Cement
MIP	Mercury Intrusion Porosimetry

Equation

DF	Durability Factor
A	Air content of hardened concrete (%)
α	Specific Surface of air voids (mm^{-1})
$\bar{L}$	Spacing factor (μm)
p	Paste content (%)
n	Number of voids per mm
S	Sorptivity ($g/mm^2 min^{0.5}$)
W	Water absorption (%)

LIST OF FIGURES

LIST OF TABLES

Chapter 1 – Introduction

The history of cement and concrete is generally assumed to have begun in ancient Egypt and Greece, although recent reports claim that it dates back as far as 9000 years ago. Natural pozzolans were used in ancient cement and concrete products, however it is relatively recently that the use of by-product mineral admixtures, such as silica fume (SF), fly ash (FA) and more recently metakaolin (MK) has become widespread. Today, mineral admixtures are attracting much attention as materials contributing to the improvement of concrete characteristics as well as to the reduction of the energy and carbon dioxide generated in the production of cement. In particular, they are indispensable for the improvement of concrete performance contributing to high strength and high durability. Concern for lack of durability is perceived as a threat to the future of concrete. Consequently, the efforts to achieve desired performance from concrete are properly those that avoid the problems generally comprehended under the title 'durability'.

The term concrete durability is used to characterise in broad terms the resistance of a concrete to a variety of physical or chemical attacks that can vary in intensity depending on the mechanisms involved. Concrete is a highly durable material in most normal, and many moderately aggressive exposure conditions. However where climatic conditions are extreme, and the surroundings are highly contaminated with chloride, sulphate and carbonate salts, widespread and premature deterioration and degradation of concrete structures can become a common occurrence, particularly if these factors are further compounded with poor quality concrete.

Concrete durability is becoming a subject of major concern in many countries, because an unusually large number of concrete structures are reported to have undergone serious deterioration. Extensive laboratory tests and field performance have confirmed that the most direct, technically sound and economically attractive *solution to overcome the problem of lack of durability of concrete is to incorporate pozzolanic and/or cementitious by-products or mineral admixtures in Portland cement concrete. The improvement in durability properties of concrete containing pozzolans is brought about by the densification of the matrix derived from filler effects and pozzolanic reaction resulting in lower permeability and thus enhanced resistance to the penetration of harmful substances.*

This chapter describes the mechanisms concerning damage resulting from freezing and thawing, outlines the basic factors affecting frost resistance in concrete and gives the research objectives of the study.

1.1 Freeze-thaw durability of concrete

Resistance to the action of freezing and thawing is a very important aspect of concrete durability. It is generally accepted that a saturated concrete without proper air entrainment, when subjected to cycles of freezing and thawing, can undergo expansion as a result of internal hydraulic pressure that is generated from freezing of water in the capillary pores and migration of water from gel pores to capillary pores. The magnitude of the hydraulic pressure depends on the permeability of cement paste, degree of saturation, amount of freezable water, the rate at which ice is formed, and the air-void spacing factor or the distance through which water under pressure must travel to seek pressure relief.

1.1.1 Action of frost

Damage to cementitious materials from freezing and thawing arises from the expansion of pore water during freezing. When ice forms in any saturated pore, tensile stresses are generated in the paste because of the 9% increase in volume experienced when water changes from the liquid to the solid state and because of the flow of water that is forced out of the pore. Because of the relatively low tensile strength of concrete (2 to 6 N/mm^2), these expansive forces need not be large to cause tensile failure, or spalling in the concrete. During thawing, water reduces in volume giving, in turn, more spaces for water absorption from the environment which may lead to further damage to concrete [Powers, 1949]. Powers and Helmuth [1953] suggested that disruptive forces are also caused by osmotic pressures. These osmotic pressures are brought about because upon freezing, part of the water in the capillary pores is transformed into pure crystals and with continued freezing the remaining water becomes more concentrated in soluble salts than the gel pore water. Osmotic pressure is therefore developed between the capillary pores and the gel structure, which may be sufficiently high to cause tensile failure. Although the action of freezing and thawing is still being debated and many other theories have been put forward to explain it [Litvan, 1972], osmotic pressure is believed to be particularly important in causing damage to concrete. Osmotic pressure arises also in connection with the use of deicer salts used on road or bridge surfaces but their negative influence is not considered in this thesis.

1.1.2 Basic factors affecting frost resistance

In order for the internal stresses to be induced by ice formation, about 90% or more of the volume of the pores must be filled with water. This is referred to as a critically saturated condition and is shown in Figure 1.1. This is because the increase in volume when water turns to ice is about 9% by volume. Concrete can be critically saturated if it is permanently exposed to water or exposed to a head of water. In other

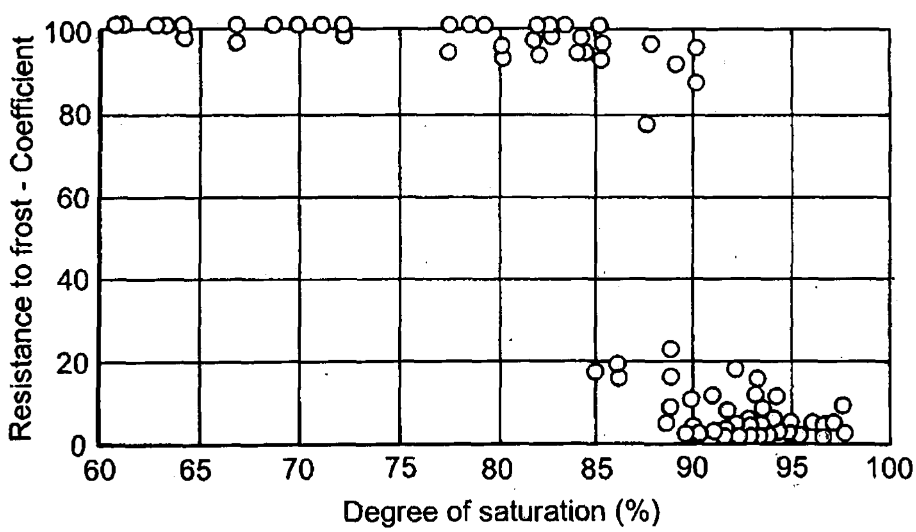


Figure 1.1 Influence of saturation of concrete on its resistance to frost [after Neville, 1995].

words, if concrete is never going to be saturated, there is no danger of damage from freezing and thawing.

Concretes which receive the most severe exposure to freezing and thawing are those which are saturated during freezing weather. Examples are hydraulic structures, e.g. parts of dams, spillways, tunnel inlets and outlets and piers, and the horizontal surfaces of exposed concrete elements, e.g. the tops and bases of walls, gutters, kerbs, driveways and pavements. Vertical concrete faces exposed to rain are rarely affected unless one face is subject to a head of water.

When concrete is subjected to aggressive external agents such as freezing and thawing, there is one way to decrease the intensity of the external aggression. This involves the reduction of porosity and permeability of concrete to slow down as much as possible the penetration of water and harmful solutions. A reduction in concrete permeability can be achieved by lowering the water/binder (w/b) ratio as much as possible. The w/b ratio has always been the controlling factor of concrete impermeability and therefore durability. A decrease of the w/b ratio decreases capillary pore volume and size, and this has a favourable effect on the freeze-thaw durability due to lower water permeability which influences the degree of saturation and lower amount of freezable water due to freeze-point depression. It is well-known that one of the prerequisites to be met in order to make a normal strength concrete frost resistant, is a maximum w/b ratio of 0.40 to 0.45.

Freeze-thaw durability of concrete has a close relationship to the concrete pore structure. There are basically two kinds of pores within the hardened mass, capillary pores and gel pores. Figure 1.2 shows a simplified model of the concrete's pores. The capillary pores range in size from approximately 5nm to 1 μm (and sometimes larger). They vary in shape but they form an interconnected system randomly distributed throughout the cement paste. These interconnected capillary pores are mainly responsible for the permeability of the hardened cement paste and thus its vulnerability to cycles of freezing and thawing. In addition to capillary pores, cement paste also contains a significant volume of gel pores. The gel pores are much smaller

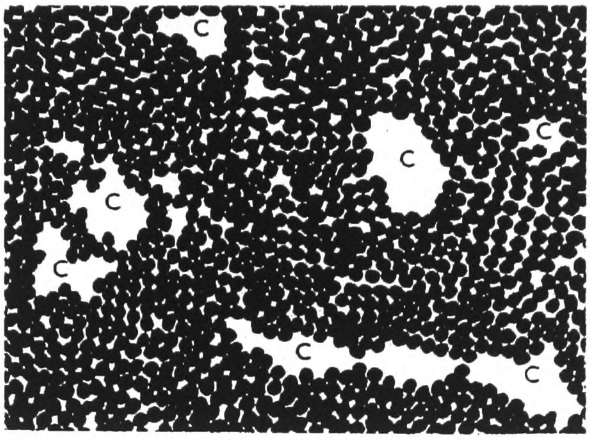


Figure 1.2 Simplified model of paste structure: solid dots represent gel particles; intersticial spaces are gel pores; spaces such as those marked C are capillary pores. [after Neville, 1995].

than the capillary pores: less than 2 or 3 nm in diameter. The aggregates, which normally represent about 75% of the volume of concrete, are also porous. These pores are generally of sizes similar to those of the larger capillary pores, but the total porosity of aggregates is usually less than 5%. Since aggregates are normally made of natural rocks and since the properties of natural rocks are highly variable, the porosity of aggregates can cover a wide range of sizes and the volume it occupies is variable.

Water in any concrete pore can freeze, but the temperature at which this phenomenon becomes possible decreases with the size of the pore. In most settled areas throughout the world, winter temperatures rarely go below -40°C, and at such temperatures gel pore water cannot freeze and ice can form in only part of the capillaries and aggregate pores. Freezing starts in larger pores in the concrete and can, at lower temperatures spread to smaller pores. As the temperature of saturated concrete is lowered, the water held in the capillary pores freezes and expansion of the concrete takes place. If subsequent thawing is followed by re-freezing, further expansion takes place so that alternate cycles of freezing and thawing have a cumulative effect. In general microcracking and subsequent increase in the permeability of concrete and degree of saturation appear to be the steps that are necessary for damage to concrete by freezing and thawing.

When concrete is air-entrained, which is achieved by incorporating into the mix an appropriate admixture called air-entraining agent (AEA), it contains a very large number of closely spaced, discrete, nearly spherical air voids. Water that is forced out of the capillaries by the pressure due to ice being formed tends to flow through the porous paste to the nearest boundary. The entrained air voids provide the concrete with escape boundaries everywhere in the paste. The effectiveness of entrained air in preventing frost disruption depends very much on the quantity and distribution of the air voids within the cement paste, since each void can protect only the surrounding materials for a certain distance. Critical considerations are therefore the volume of air-entrained, and since this must be evenly dispersed, the air voids spacing and size. Current specifications generally require the air content to be within a narrow range - around 4 to 7 percent of the total concrete volume. Another important parameter which is directly related to the size of the air voids is specific surface. This value represents the surface area of the air voids divided by their volume. However the most important parameter for good protection against frost is half the average distance between the outer boundaries of two adjacent air voids so called the "spacing factor". It has been confirmed both by laboratory data and field experience that a spacing factor of 200 μm appears to be a good design value.

The total volume of voids has a detrimental effect on strength, and as close spacing is required it follows that the smaller the air bubbles the better. Entrained air voids are distributed over a range of sizes as shown in Figure 1.3, generally from 0.005 mm to 1 mm in diameter. An effective air void system has a large number of these small bubbles dispersed uniformly throughout the cement paste. Air in concrete can also be accidentally entrapped due to incomplete compaction. The void size of this type of air is characteristically 1 mm or more and irregular in shape.

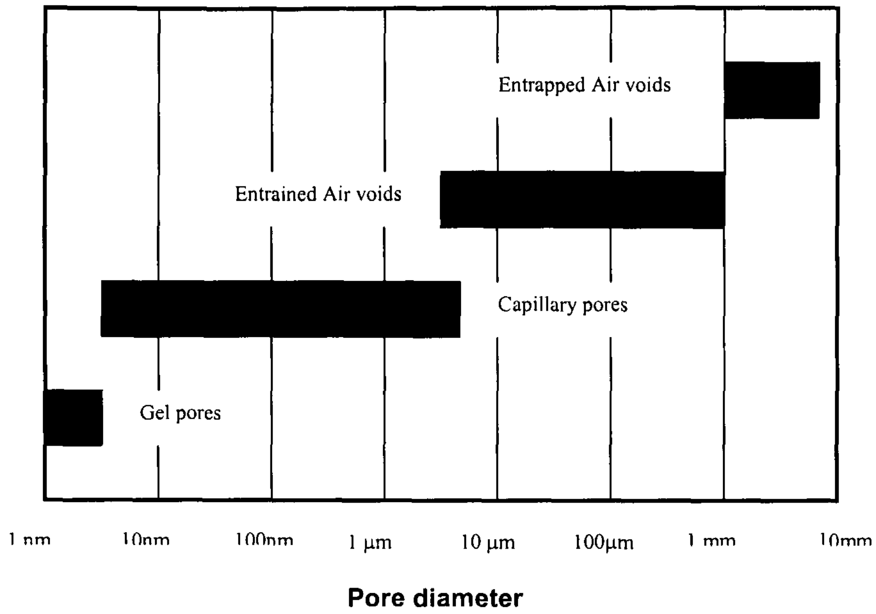


Figure 1.3 Range of pore sizes for the four basic categories of pores in concrete.

1.2 Research objectives

To improve the performance of concrete, numerous new technologies and products have been developed. Notable among these is high strength concrete containing mineral admixtures in combination with an appropriate and compatible high range water reducing admixture (HRWRA) or as more commonly known superplasticizer (SP). It has long been a concrete technologist's dream to discover a method of making concrete at the lowest possible w/b ratio while maintaining high workability. To a considerable extent this dream was fulfilled with the advent of SPs.

One method for reducing the risk of deterioration due to the action of freezing and thawing, apart from air entraining, is to reduce as much as possible the capillary porosity (or sorptivity) and thus amount of freezable water present. This can be done by using mixtures with w/b ratios that are as low as possible. In such instances the use of SPs may permit production of concrete, that will have very little capillary porosity. The use of mineral admixtures like SF, FA and MK is another possible alternative which obviates the need for very low w/b ratios. The beneficial action of these materials on decreasing permeability has been well explained and attributed to several mechanisms, such as the filler effect and pozzolanic action. For example MK increases the pore fineness of the bulk cement matrix [Khatib and Wild, 1996] and thus results in a less permeable concrete. However SF and MK produce a substantial reduction in workability at high replacement levels, as a result of their high specific surface. For this reason SPs are a necessity for mixtures incorporating these mineral admixtures.

As SPs began to be used in large quantities in Europe about 20 years ago, the question arose as to whether freeze-thaw resistant superplasticized concrete could be produced by combining SPs with air entraining agents. Superplasticizers can also be useful as far as freeze-thaw is concerned. They can be used to reduce the amount of mixing water without changing the cement content in order to reduce the w/c ratio and therefore not only increase strength and reduce sorptivity and water absorption but also improve freeze-thaw durability. They are capable of allowing reduction in the w/c ratio to the low levels (0.40-0.45) required for frost resistant concrete of appropriate workability by American and European specifications. In addition, the use of chemical admixtures and mineral by products, such as SF and FA, has become relatively common in recent years. This thesis addresses the freeze-thaw durability of superplasticized air-entrained and non air-entrained concrete incorporating mineral admixtures.

Concrete structures are being increasingly subjected to hostile and aggressive environments, such as marine, salt contaminating, arctic and hot arid environments. Examples of serious deterioration of concrete in modern structures include seafloor tunnels, offshore piers and platforms, highway bridges, sewage pipes, and railway sleepers. The requirements for acceptable durability in such conditions go beyond those achievable with ordinary cements. As a result, the blending of Portland cement (PC) with pozzolanic materials has become an increasingly accepted practice in such structures.

However, while SF and FA are widely used and their related literature is abundant, MK has been to date much less studied, although interest in its durability performance and applications have been growing in the last few years. The use of

MK as a pozzolanic additive for modern cement and concrete has not been very popular. This is due to its relatively high cost compared to that of other pozzolanic materials such as FA. Nevetherless, the usefullness of MK as a mineral admixture for cement and concrete is well demonstrated e.g. Sabir et al. [2001]. Numerous publications can be found in the literature dealing with MK's influence on the microstructure of concrete and consequently on some of the properties which directly relate to durability. For example, MK improves the compressive strength [Wild et al., 1996], reduces the transport of water and salts through the sample [Kostuch et al., 1993] and prevents alkali-silica reaction from occurring [Ramlochan et al., 2000]. To date there are only a few reports in the literature on the air entrainment and freeze-thaw durability of concrete incorporating MK [Zhang and Malhotra, 1995]. The work reported in this thesis is an attempt to fill this gap.

Moreover, much of the published data, relate to the use of SF, FA or MK, alone as partial replacement of, or as an addition, to PC. The major drawback of using FA as partial cement replacement material is the low and slow development of early strength, whereas high SF or MK contents can lead to problems of dispersion and workability because of their high water demand. Furthermore, there is some growing evidence that concrete incorporating FA or SF alone cannot give the range of properties required for long-term durable concrete in extreme environments such as those in arctic regions. The approach adopted in this study to achieve improved freeze-thaw performance was to use a constant PC content with selected mixes of FA, MK or combinations of FA and MK and to examine the role and effectiveness of such mixtures in improving the strength, pore structure, air void system and consequently the frost resistance of the resulting concrete. For comparison purposes some mixtures contained SF.

1.3 Thesis structure

In addition to the introduction the thesis contains six Chapters. Chapter 2 contains a review of the literature relating to the air entrainment, freeze-thaw performance and microstructure of concrete containing pozzolanic materials. A description of the materials used throughout the research and the experimental methodology followed can be found in Chapter 3. The results from the various investigations undertaken are presented in Chapters 4, 5 and 6 together with concluding remarks for each Chapter. Finally, Chapter 7 gives a synthesis of the main findings of the research and presents conclusions drawn from the research along with recommendations for further investigations.

Chapter 2 – Review of literature

This chapter starts with a general information section on air-entraining agents and superplasticizers with some emphasis on their mode of action. It continues with a brief overview of the effect of mineral additives like SF, MK and FA on air entrainment and possible explanations for their behaviour are presented and discussed. The roles of the air void characteristics of the concrete microstructure played on the concrete's resistance to freeze-thaw action are outlined. The influence of SPs on these characteristics and subsequently on freeze-thaw durability of concrete is also explained. The chapter continues with a detailed review of investigations on freeze thaw durability of concretes incorporating SF or MK or FA with some emphasis on the mechanisms involved in their frost resistance.

Most of the important properties of hardened concrete are related to the porosity and pore size distribution of the hydrated cement paste. Engineering properties, such as strength, shrinkage, creep, permeability together with durability related properties like damage from freezing and thawing are directly influenced or controlled by the relative amounts of the different types and sizes of pores. A brief review of the influence of pozzolans on pore sizes and pore size distributions is also presented.

Finally the chapter concludes with a brief overview of the influence of pozzolans like FA and SF on the water absorption properties of concrete. Two aspects of the water absorption characteristics of porous construction materials are of particular interest and practical significance [Wilson et al., 1999]. These are the total water absorption and the capillary suction properties, or sorptivity of the materials.

2.1 Air entraining and superplasticing admixtures

After compaction, normal concrete is likely to contain about 1-2% air by volume. This accidentally entrapped air is unevenly distributed and consists of bubbles of irregular size and shape. There is another distinctive difference between air voids accidentally entrapped in concrete and the deliberately entrained air bubbles. The latter are very much smaller, typically 50 μm in diameter whereas the former can be as large as the familiar, albeit undesirable, pockmarks on the formed surface of concrete. Numerous types of air entraining agents are available in the market with the vinsol resin based products being the most common. Others include alkyl aryl sulphonates, alkyl sulphates and salts of fatty acids derived from animal and vegetable fats and oils. The optimum dosage for AEAs is usually below 1% by mass of cement.

Air-entraining agents are admixtures capable of forming air bubbles dispersed throughout the cement matrix that binds the aggregates. They introduce a controlled amount of air in the form of millions of bubbles of uniform size and that are uniformly distributed throughout the concrete mix. The common feature of the air-entraining chemicals is that they are all surface active agents, or surfactants. This means that they function by interacting at the interfaces between the air, water, cement and aggregate in the concrete mix. The basic structure of air-entraining surfactants is that of a long-chain molecule with a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail (see Figure 2.1(a)). This causes the surfactant molecules in an agitated solution to orientate at the air-water interface with the polar head attracted towards the dipole charges on the water molecules and with the organic, non-polar tail towards the air. This has the effect of reducing the surface tension of the water and thereby stabilizing bubbles that are formed when the solution is agitated. The air-entraining agent also acts on the cement and aggregate surfaces with the reverse orientation to that at the surface of the air bubbles so providing additional stability to the air void system (see Figure 2.1(b)).

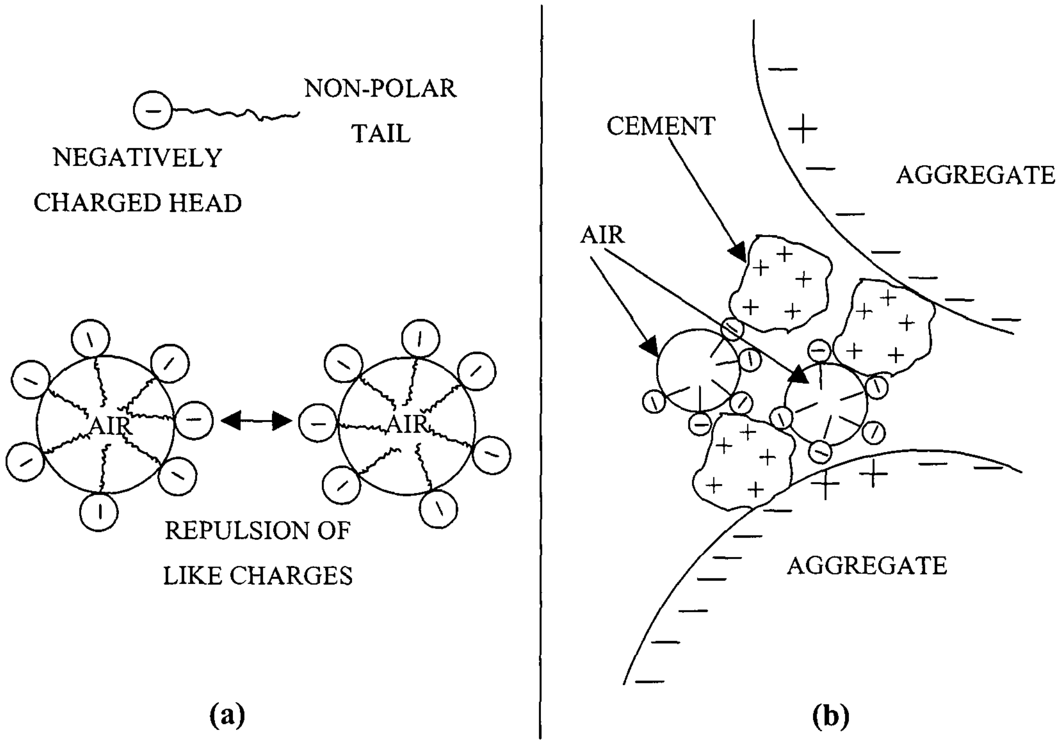


Figure 2.1 (a) The anion of air-entraining agent and the orientation of surfactant at air bubble surface (b) mechanism by which entrained air voids remain stable within concrete.

Superplasticizers are concrete admixtures which can be mainly used either to increase the workability of fresh concrete at a given mix composition or to reduce the amount of mixing water and w/b ratio for a given workability in order to increase strength and durability. For instance to compensate for the loss of workability in mixtures like those containing pozzolanic materials such as SF and MK, or even increase the water reduction effect of FA superplasticizers are normally used. Due to addition of superplasticizers the slump increase at a given mixture composition can be 150-200 mm and the reduction of mixing water at a given slump can be up to 30%, both depending on the method of addition, dosage and type of admixture used. Presently the most important SPs available are based on condensed melamine sulfonated formaldehyde (MSF), naphthalene sulfonated formaldehyde (NSF) or lignosulphonates in the form of 40% aqueous solution to facilitate an accurate, reliable, and automatic dispensing at the batching plant. The optimum dosage of commercial SPs is in general in the range 1-2% by mass of cement.

Superplasticizers consist of very large molecules which dissolve in water to give ions with a very high negative charge. The main action of these molecules is to wrap themselves around the cement particles and give them a highly negative charge so that they repel each other. This brings about a rapid dispersion of the individual cement grains. In doing so, water trapped within the original floccs is released and can then contribute to the mobility of the cement paste and hence to the workability of the concrete.

2.2 Air entrainment in concrete incorporating pozzolans

To improve freeze thaw durability of concrete, air in the form of closely spaced minute bubbles is introduced in the whole mass of concrete by using AEAs. With the increasing use of pozzolans i.e. FA and SF, as cement replacement materials it is important to understand how the air entrainment process is affected by such additions. Current knowledge concerning the specific interaction of AEAs with various materials is insufficient to predict their behaviour in advance of preparation of a concrete batch. FA may make the problem of air entrainment much more complicated as it may affect both the air content and the stability of the air voids [Ashby, 1982, Gebler and Klieger, 1983].

Laboratory as well as field studies have revealed that the addition of some FAs cause an abnormal increase in the amount of AEA required to produce a given level of air entrainment in concrete [Larson G, 1953, Pasko and Larson, 1962, Zhang, 1996]. It has even been reported that some FAs make it impossible to entrain a specified amount of air [Samarin et al., 1983]. In one investigation by Carette and Malhotra [1983a], the air entraining admixture dosage needed to entrain 6.4% air in concrete increased from 170 ml/m^3 for control concrete to 690 ml/m^3 for concrete incorporating 60% FA as PC replacement. This was an extreme case and in general the increase was considerably less. In a more recent study Dhir et al. [1999] found that air contents of up to 4.5% (using vinsol resin type air entraining agents) in concretes containing FA required an increase in the admixture demand of a factor in excess of two relative to the control PC concrete mixes.

The erratic interaction of FA with air entraining agent has undermined the efforts of several researchers [Larson T, 1964; Gebler and Klieger, 1983, Sturrup et al., 1983, Hill et al., 1997] in their attempt to explain the underlying mechanism. Based upon test observations it is generally accepted that fineness of FA and carbon content expressed as percentage loss on ignition (LOI) in FA play a predominant role in increasing the AEA demand of FA concrete. The presence of organic substances other than carbon may also interact with the AEA thus reducing its effectiveness.

FA is normally finer than cement and the volume added is usually greater than the volume of cement replaced to produce FA concrete. As a result the surface area of the total constituents in concrete increases and thus a greater volume of AEA is needed to provide the same surface concentrations of the active air entraining ingredient. This increase of fines explains the increase of AEA dosage required with increasing amounts of the FA observed by many researchers [Zhang, 1996, Dhir et al., 1999]. In addition tests showed that concrete containing FA has its percentage entrapped air content reduced by 0.5 to 1 due to the influence of the fines [Lane, 1983, Sturrup et al., 1983]. The second phenomenon possibly responsible for the increased AEA requirement is related to the carbon content of FA. The carbon, due to its high surface area, adsorbs a portion of the AEA which makes it unavailable for creating the required conditions for stable air bubbles. This results in higher dosage requirements to obtain a specified air content. The amount of adsorption varies with the magnitude of carbon present and possibly with the form of such carbon. Sturrup et al. [1983] found that there is a good correlation between the total carbon content of FA concrete and the amount of admixture required to entrain 6.5 ± 1% air. It was specifically indicated that doubling the carbon content required a double dosage of AEA. Gebler and Klieger [1983] showed that a different amount of air entraining agent is usually needed for a particular air content with FAs of different characteristics. If the quantity of organic substances, carbon content and LOI of the FA increases, then more AEA is required for a specified air content. Similarly Dhir et al. [1999] showed that higher demands for AEA were observed for FAs with increasing LOI. It was also found that for the FA concrete the AEA remains inactive beyond a level of addition of approximately 250 ml per 50 kg of binder since air content remained constant at 5.5% with increasing amounts of the AEA. This effect would appear to reflect the known influence of carbon particles present in FA and their significant adsorption capacity for AEAs [Gebler and Klieger, 1983], thereby increasing demand until this consumption process ceases on saturation; entrainment of air can occur normally thereafter.

Not only FA, but also other mineral admixtures such as SF cause increase in AEA demand [Okkenhaug and Gjorv, 1982] because as explained above they are much finer than PC. According to Carette and Malhotra [1983b] the dosage of air-entraining admixture to produce a required volume of air in concrete usually increases with increasing amounts of SF due to the very high surface area of silica fume and to the effect of carbon when it is present. In another series of experiments Carette and Malhotra [1983a] found that for low w/b ratio (= 0.40) the replacement of cement by SF in superplasticized concrete led to an increased need for AEA to maintain the same air content. Carette and Malhotra [1983a] concluded that entrainment of more than 5% air is difficult in concrete incorporating high amounts of SF, even in the presence of a SP.

In a further test series Lehtonen [1985] studied concrete of w/b = 0.45 with 0, 5, 10, and 15% SF, and found that a higher dosage of air entraining agent was needed to produce equal amounts of air with increasing SF dosage. Carette et al. [1987] reported that the required dosage of air-entraining admixture increased with the amount of SF, especially for concrete made with a w/b ratio of 0.40 against others with w/b ratios of 0.5 and 0.6. An investigation by Sabir and Kouyiali [1991] has also shown that in using a fixed dosage of air entraining agent, the resulting volume of air decreased appreciably with increasing SF content. The air content reduced from 6.6% for the control mix to 4.4% for the mix incorporating 12% SF.

Toutanji [1998] performed an experimental study on the properties of SF concrete containing air-entraining agent. The SF content ranged from 0 to 20% by mass of the binder. The fresh mix properties were characterized by slump and air content tests. The test results showed that air entrainment improved the workability of SF concrete, however the effectiveness of air entrainment reduced with increasing SF content. It was also found that the increase in air content in both control and SF concrete due to addition of air entrainment decreases with increasing air-entraining agent. More specifically, employing a dosage of 0.05% (as percentage of the binder) had considerably more effect on air content than increasing the dosage from 0.05 to 0.10%.

MK, like SF, is an ultra-fine highly active pozzolan, that might be expected to behave in a similar manner to SF when replacing PC in concrete. To date limited findings [Zhang and Malhotra, 1995] showed that at the replacement level of 10%, MK concrete required a similar amount of AEA as SF concrete to entrain a similar amount of air. Air entrainment in mixtures incorporating such ultrafine pozzolans becomes even more complicated with the addition of SPs in order to compensate for the loss of workability attributed to the very fine particles of these materials. In the same study Zhang and Malhotra, [1995] found that MK concrete required almost as much SP as the SF concrete in order to achieve similar slump, although findings by other researchers [Caldarone et al., 1994, Caldarone and Gruber, 1995] showed a lower requirement for SP.

Seen as a whole the replacement of cement with SF results in reduced air contents relative to the control concrete. However the variability due to SF addition is relatively less pronounced than with FA concrete [Virtanen, 1983]. Achieving the required air content necessitates an increase in the AEA dosage, but AEA demand decreases in the presence of a SP [Langan et al., 1990] or a plasticizer [Okkenhaug and Gjorv, 1982]. The increased demand for AEA in SF concrete can be directly correlated to the specific surface increase of SF-cement blends. SF particles are smaller than those of PC and addition of SF, therefore, increases the fine fraction of the particles. The higher fraction of smaller particles then increases the surface area causing greater binding of the water in the mixtures. This removes water required for the air void formation. Also, as SPs increase the fluidity of the paste, they tend to enhance the air-entraining effect of AEAs, thus the decreased demand for AEA in the presence of SPs [Langan et al., 1990].

2.3 Freeze-thaw resistance of concrete

Decisions regarding the freeze-thaw resistance of concrete are often based on laboratory freeze-thaw testing rather than an established field performance. The freeze-thaw resistance of concrete has commonly been determined by one of the following laboratory procedures:

- **Method 1 (ASTM C666, 1997, Procedure A)-** By rapid freezing and thawing of the concrete whilst it is immersed in water. The cooling rate ranges from 6 to 15°C/hour, with a minimum temperature of -18°C.
- **Method 2 (ASTM C666, 1997, Procedure B)-** By rapid freezing of saturated concrete in air and thawing whilst immersed in water. The cooling rate ranges from 6 to 15°C/hour, with a minimum temperature of -18°C.
- **Method 3 (BS 5075: Part 2, 1982)-** By freezing and thawing of air-entrained concrete whilst immersed in water. The total air content of the concrete is 5.5% by volume. The cooling rate ranges from 1.4 to 3.3°C/hour, with a minimum temperature of -18°C.

In this review the laboratory data discussed were primarily obtained using the ASTM C666 methods. In these methods freeze-thaw durability is given by a durability factor (DF) given by:

$$DF = PN/300$$

where P is the relative dynamic modulus of elasticity at N cycles and N is the number of cycles at which P falls below 60%. The concretes are subjected to a maximum of 300 freeze-thaw cycles.

2.3.1 Required air void system parameters

The three basic parameters used to describe the characteristics of the air-void system in hardened concrete are:

- The air content (A)
- The specific surface of the air voids (α)
- The spacing factor of the air voids ($\bar{L}$)

The most important parameter of the air-void system is the spacing factor of the air voids. The most obvious question that can be asked concerning frost resistance is what value of the spacing factor is necessary to protect concrete against frost damage? Powers [1949] mentioned the value of 250 μm, and later [Powers, 1954], published results from rapid freezing and thawing tests carried out in his laboratory that indicated that this value was applicable to relatively wide range of concretes. Backstrom et al. [1958] stated, again on the basis of rapid freezing and thawing tests, that the required value varies between 100 and 200 μm, depending on the type of concrete. Since then a limit of 200 μm on the spacing factor has been specified in the USA by ASTM C260-95 [1995]. It is the range of values of 200-250 μm that was subsequently adopted by many regulating bodies and agencies and that are now the most widely recognised values. A spacing factor of 200 μm or below will also protect concrete against scaling due to freezing and thawing in the presence of de-icing salts [Pigeon and Pleau, 1995], although in one case, in Germany, it was found that spacing factors between 200 and 250 μm can lead to scaling on roads [Sommer, 1979].

The air content of fresh concrete is usually measured by the pressure method and in most countries that value of the air content serves as an acceptance criterion for concrete. If the value is lower than the specified range (generally 5-7% for concrete with 20 mm nominal size aggregate), it is rejected. Figure 2.2 [Saucier et al., 1991] shows the relationship between air content measured in fresh concrete and that subsequently measured in hardened concrete for a large number of laboratory and field mixes. These test results indicate that in the normal range of air contents (2-10%), the two values are generally in good agreement. The differences that do occur can be due to numerous causes [Hover, 1989, Saucier et al., 1991]:

- There are normal statistical variations due to concrete heterogeneity

- Concrete in the pressure meter is not necessarilly compacted in the same way as the specimens used for microscopical examinations
- Air voids in these specimens can collapse before setting, or the air in the smaller air voids can be dissolved in water
- The hypothesis on which the pressure method is based is not necessarily always valid

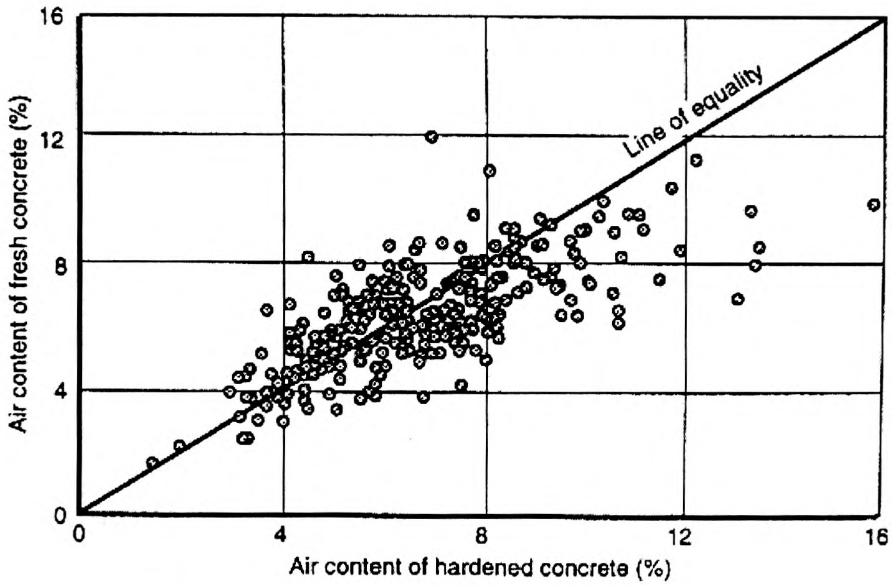


Figure 2.2 Relationship between the air content measured in fresh concrete (using the ASTM C231 pressure test method) and the air content measured in hardened concrete (using the ASTM C457 microscopical examination) [after Saucier et al., 1991].

As regards frost resistance it is the spacing factor that is most important, not the air content. It is therefore important to evaluate whether the air content measured in the fresh concrete can provide a reasonable estimate of the value of the spacing factor. The relationship between air content and mean air-void spacing factor is scattered [Saucier et al., 1991] as shown in Figure 2.3. For instance, at an air content of 6%, spacing factor values range between 100 and 400 μm approximately, depending on the specific surface or the average size of the air voids. Furthermore the spacing factor is influenced by w/c ratio (the size of the air voids decreases with reducing w/c ratio) or cement content, the use of SPs (melamine or naphtalene based [Kobayashi et al., 1981], the grading of the aggregates, the characteristics of the mixer and the temperature of the mixture [Gay, 1983, 1986]. Despite the number of parameters affecting the value of the spacing factor, the dosage of AEA is the most important parameter that controls the value of the air void spacing factor, at least in normal concrete mixtures [Saucier et al., 1991]. Figure 2.4 shows the results from a series of tests performed on a large number of laboratory and field concretes.

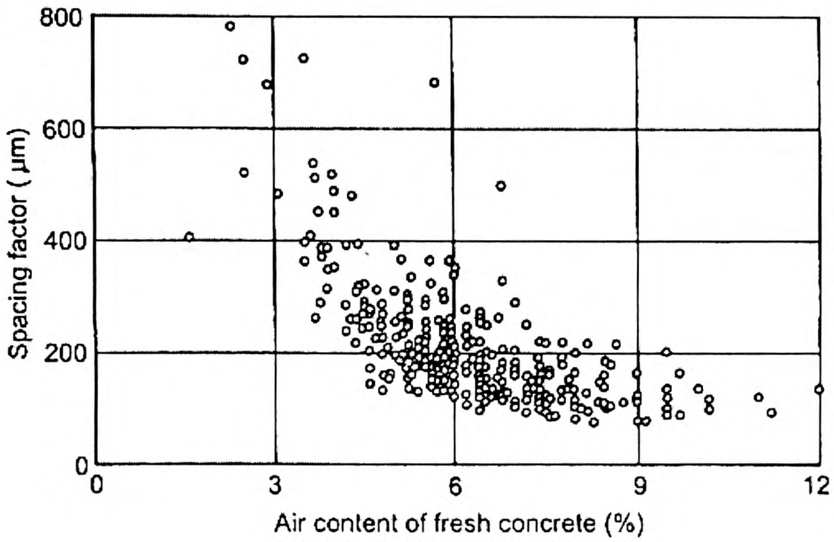


Figure 2.3 Relationship between air content measured on fresh concrete and air void spacing factor in hardened concrete [after Saucier et al., 1991].

Some investigators [Mielenz, 1968, Gjorv et al., 1978, Mather, 1978] have found, contrary to others [Powers, 1954, Backstrom, 1958, Pigeon, 1989] that the correlation between frost damage and air void spacing factor is not always very clear. A number of investigators have concluded that for a given air volume concentration, freeze-thaw resistance is related to air-void spacing, the smaller the air-void spacing or the smaller the air-void size, the greater the freeze-thaw resistance. This is illustrated in Figure 2.5. Dhir et al. [1999] indicated that excellent freeze-thaw durability was obtained in concretes of spacing factor up to 400 μm and that the performance declined at spacing factors above this. The spacing factors required for good freeze-thaw durability were slightly higher than those that have been reported in the literature specifying durable concrete for frost conditions (200 μm) [Gebler and Klieger, 1983; Roberts and Scheiner, 1981] but they are in line with values given in other studies [Kobayashi et al., 1981; Pigeon and Lanchance, 1981]. It would appear that the differences in spacing factor values and the specification relate to different rates of freezing during testing [Pigeon and Lanchance, 1981]. In general, faster freezing rates give serious damage at lower spacing factors.

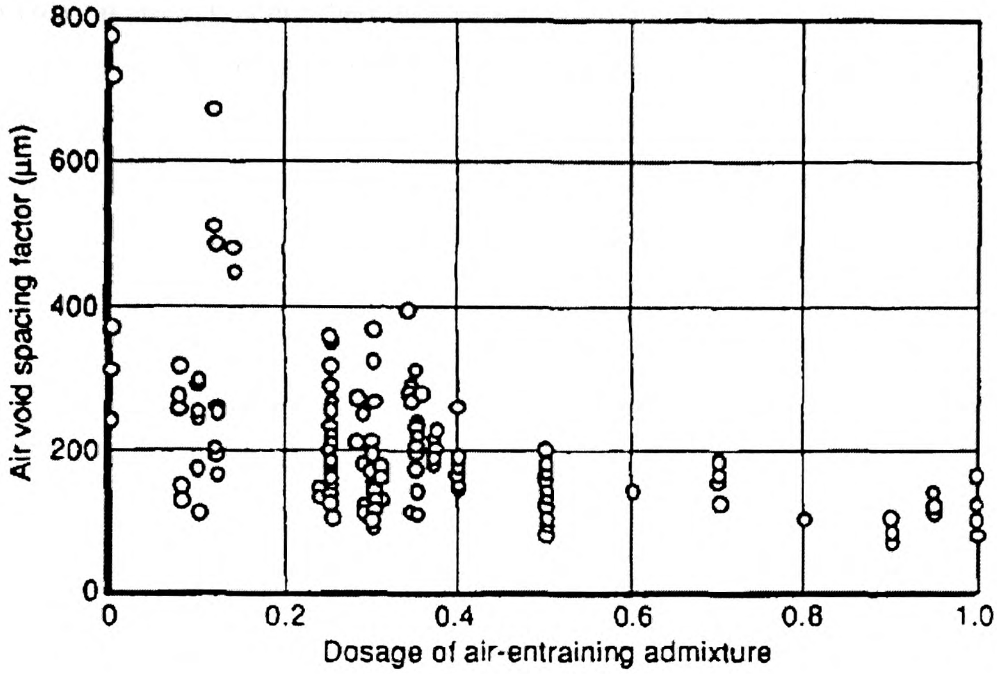


Figure 2.4 Relationship between air-entraining agent dosage and spacing factor [after Saucier et al., 1991].

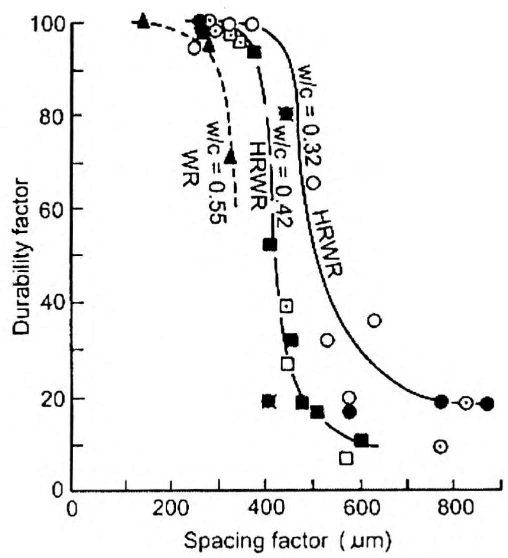


Figure 2.5 Relationship between spacing factor and durability factor in concrete containing high range water-reducing admixture [after Kobayashi et al., 1981].

As can be seen in Figure 2.6 which shows a polished section of air-entrained concrete at 16x magnification, air voids cover a large range of sizes. Most air voids in air-entrained concrete are in the 10-100 μm range, but they can be as large as 1 mm (see Figure 1.3). Published data indicate that the number of air voids smaller than 10 μm is not very important [Pleau et al., 1990]. Hover [1988] has calculated that, theoretically, air voids smaller than 10 μm cannot exist because in such air voids the internal pressure, that in effect balances the surface tension, becomes higher than the pressure required to dissolve the air in water. Figure 2.7 shows the distribution of air-void sizes in a typical air-entrained concrete. This distribution was obtained by measuring the diameter of the intercepted air voids on a polished concrete section. It does not, however, represent exactly the real distribution of air void sizes because statistically the larger air voids are more likely to be intercepted than the smaller ones. The figure shows clearly that the average size of air voids in air-entrained concrete is of the order of 50 μm.

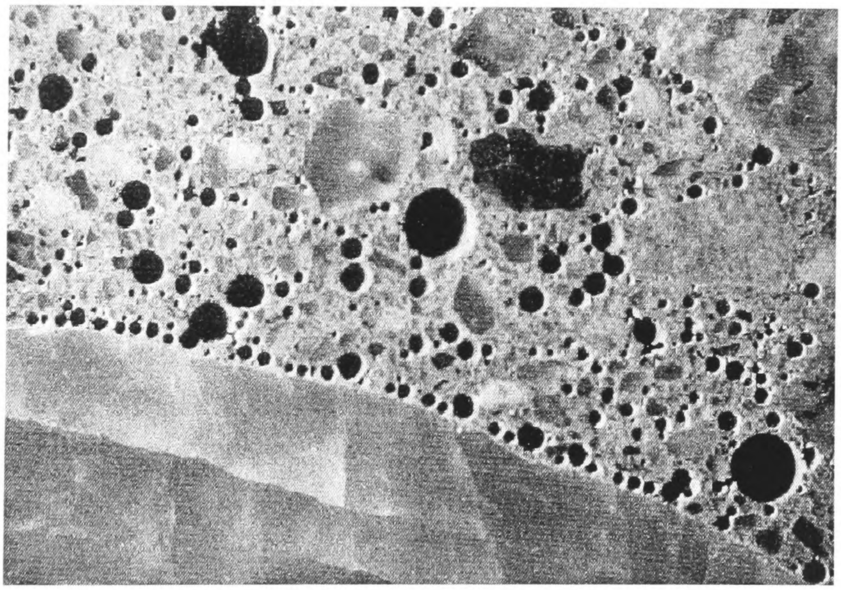


Figure 2.6 Typical air voids in an air-entrained concrete specimen (7.5%) examined under an optical microscope at a magnification of 16X [after Dodson, 1990].

Much of the air entrapped in concrete due to incomplete compaction is unsuitable for enhancing the freeze-thaw resistance of concrete. This is because both the air-void size and spacing are too large. However it should not be forgotten that accidental entrapped air is present in any concrete, whether entrained or not, and, as the two kinds of voids cannot be distinguished other than by direct observation, the specific surface represents an average value for all voids in a given cement paste. For air-entrained concrete of satisfactory quality, the specific surface of voids is in the range of approximately 16 to 24 mm^{-1}, but sometimes it is as high as 32 mm^{-1}. By contrast, the specific surface of accidental air is less than 12 mm^{-1} [Powers, 1954].

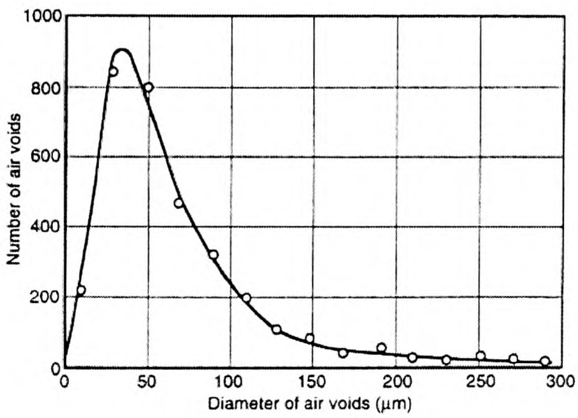


Figure 2.7 Size distribution of the diameter of air voids observed on a polished concrete section for a typical air-entrained concrete [after Pleau et al., 1990].

2.3.2 Superplasticizers and freeze-thaw resistance

In the last 20 years, the freezing and thawing durability of superplasticized concretes has been widely investigated, but still remains a controversial topic. At first, many studies indicated that air-entrained, superplasticized concretes with normal w/c (0.40-0.50) when subjected to rapid freezing and thawing cycles, have a generally good resistance to such cycles, even when the values of the spacing factor were in the 200-400 μm range [Malhotra, 1981a, Malhotra, 1982, Malhotra, 1981b], and it was suggested that superplasticizers possibly enhance the freeze-thaw durability of concrete [Plante et al., 1989, Saucier et al., 1990]. However, a recent study [Pigeon and Langlois, 1991] clearly indicates that SPs have no real influence on the intrinsic resistance of concrete to internal microcracking due to rapid freezing and thawing cycles. The fact that air-entrained, superplasticized concretes often have a spacing factor higher than the generally accepted 200-250 μm limit for the usual range of air content (5-8%), as many studies have shown, indicate that it is not necessarily detrimental to the resistance to freezing and thawing cycles.

In fact, the real influence of SPs on the frost durability of concretes with normal w/c ratios is related to air entrainment. Laboratory and field studies both indicate that SPs often modify the characteristics of the air void system. Superplasticizers can affect the air-void system in two ways. First, they increase the paste fluidity which can facilitate air-void coalescence. Second, they increase the repulsive forces between the cement grains and can thus weaken the shell of cement paste that protects the air voids from coalescense. Attention was first drawn to the total air content which was often found to be higher after the addition of a superplasticizer [Malhotra 1981b, MacInnis and Racic, 1986] although air losses were also encountered [Malhotra 1981b, Tognon and Cangiano, 1982]. Since the use of SPs generally tends to produce a higher air content, the dosage of the air entraining admixture is normally reduced in superplasticized, air-entrained concretes (with 5-8% air content) [Langan et al., 1990], which thus generally have spacing factors in the 300-400 μm range, i.e. higher than the usual 200 μm value for non-superplasticized, air-entrained concretes.

Further studies have revealed that SPs seem to facilitate the entrainment of larger voids since, most of the time, the mean diameter of air voids was increased and the specific surface correspondingly reduced [Malhotra, 1981b, Roberts and Scheiner, 1981, Mielenz and Sprouse, 1979, Litvan, 1983, Pigeon et al., 1989, Plante et al., 1989, Saucier et al., 1990]. The presence of the larger air voids in superplasticized concretes results in a smaller specific surface and consequently in a larger spacing factor for a given air content. Figure 2.8 [Pleau et al., 1990] shows the size distribution of the air voids in a normal air-entrained concrete (with a spacing factor of 398 μm and in superplasticized air-entrained concrete (with a spacing factor of 387 μm). The two distributions showed that although superplasticized concrete had a little coarser size distribution than plain concrete, the size distribution was not affected by the presence of the SP. Other studies indicated that SPs can have a detrimental effect on the stability of the spacing factor and of the other characteristics of the air void system [Pigeon et al., 1986, Pigeon et al., 1987] but further analysis on the subject falls beyond the scope of this thesis.

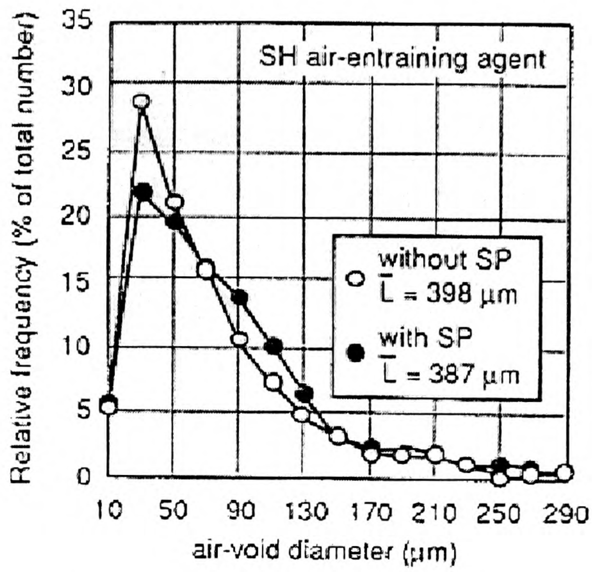


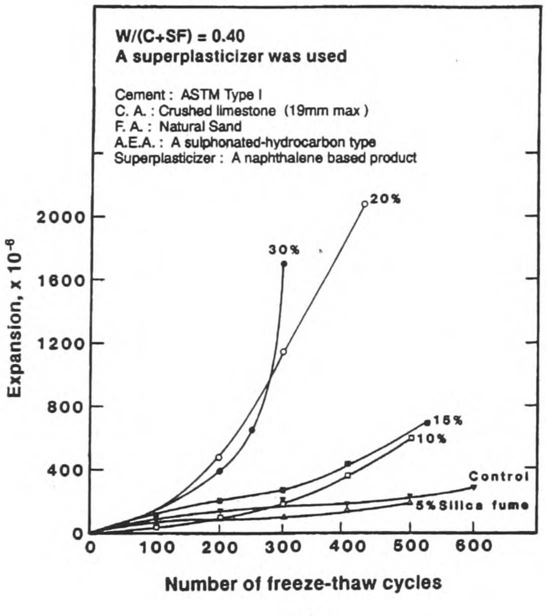
Figure 2.8 Influence of superplasticizers on size distribution of air voids [after Pleau et al., 1990].

2.3.3 Freeze-thaw resistance and pozzolans

Several investigations have been carried out on the durability of SF or FA concrete exposed to freezing and thawing and although considerable data are now available on this subject, some of the findings have been inconclusive and at times, contradictory. This is not surprising in view of the number of factors that have considerable influence on the performance of concrete with respect to frost action. These include cement content, pozzolan replacement level, w/b ratio and whether or not SPs and AEAs are employed. Furthermore, curing conditions, age and moisture states [Sellevold and Farstad, 1991] of the concrete at the time of exposure are important considerations. The difficulties associated with the diversity of the parameters and conditions involved are compounded by the lack of agreement on the method and media of testing and the duration of exposure to freezing and thawing. In the main, the studies have been conducted following procedures suggested by ASTM C666-97 [1997].

Silica fume concrete

Several investigators have performed studies on the freezing and thawing resistance of SF concrete. These include, among others, Gjorv [1983], Virtanen [1983], Malhotra and Carette [1982], Malhotra [1984], Pigeon et al. [1986], Yamato et al. [1986], Sabir and Kouyiali [1991], Batrakov et al. [1992], Hooton [1993] and Sabir [1997]. The freezing and thawing test results for one such study [Carette and Malhotra, 1983a] are shown in Figure 2.9. The air-entrained concrete incorporated



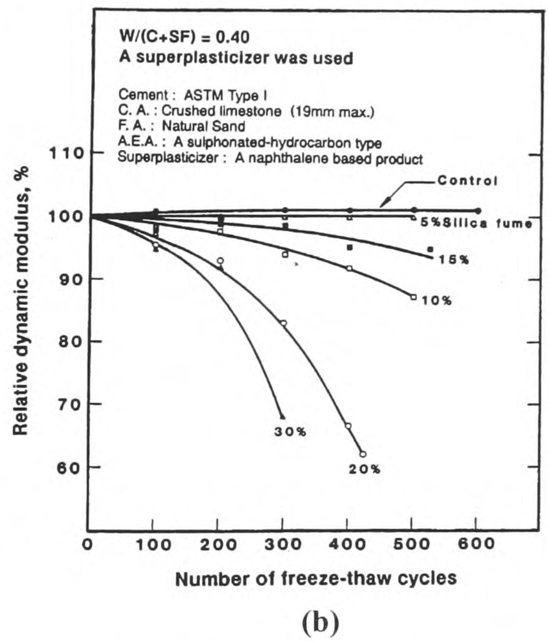


Figure 2.9 Expansion and relative dynamic modulii of test prisms after freezing and thawing exposure (ASTM C666 Procedure A) [after Carette and Malhotra, 1983a].

up to 30% SF by mass as replacement for PC. The w/b was maintained at 0.40 and any loss in slump due to the use of SF was compensated by the use of naphtalene-based SP. The test data revealed satisfactory performance of air-entrained concrete except for those concretes which contained 20 and 30% SF. In this investigation it was found that air-entrained concretes without and with 5% SF showed much lower air void spacing factors than those containing 10-30% SF although all the concretes had approximately the same air content in the fresh state (4-5%). Excessive expansions and low values of the relative dynamic modulus indicative of the poor freeze-thaw performance of concretes incorporating 20 and 30% SF could not be explained in terms of the high values of the spacing factors, because concretes containing only 10% and 15% SF also had high spacing factors. The author speculated that the poor performance of the concretes in question, was due to the high amount of SF resulting in a very dense cement matrix that did not permit internal movement of water.

In another investigation, the freezing and thawing resistance of non air-entrained and air-entrained concrete incorporating various amounts of SF was compared [Malhotra, 1984]. Once again, the air-entrained concrete incorporating 30% SF failed to meet the durability criterion, although in this case the poor performance of the concrete was attributed to the unsatisfactory spacing factor values. The above study led to the conclusion that non air-entrained concrete, regardless of the w/b ratio, and irrespective of the amount of SF shows very low DFs and excessive expansion when tested in accordance with ASTM C666, Procedure A or B. The concrete also appears to show somewhat increasing distress with increasing amounts of SF. The air-entrained concrete, regardless of the w/b ratio and containing up to 15% SF as partial replacement for cement performed satisfactorily under both procedures. However, concrete incorporating 30% of SF with a w/b of 0.42, performed very poorly (DFs less than 10%) irrespective of the procedure used.

Malhotra et al. [1986] reported results of another investigation dealing with freezing and thawing resistance of concrete in which non air-entrained concrete was proportioned to have w/b ratio ranging from 0.25 to 0.35. One series of the mixtures incorporated 10 to 20% SF. The non air-entrained concrete test specimens, with and without SF, when exposed to rapid freezing and thawing tests (ASTM C666, Procedure A) started showing distress at less than 30 cycles, developed major cracks at 50 cycles but no scaling was observed in any instance. However visual observations on the surface of the specimens indicated that the prisms without SF had performed marginally better. Data by Hammer and Sellevold [1990] were generally in agreement with the above data [Malhotra et al., 1986].

Yamato et al. [1986] using the method of ASTM C666-Procedure A, tested concretes with w/b ratios of 0.25, 0.35, 0.45 and 0.55, and PC replacements by SF of 5, 10, 20, and 30%. Except for the concrete with w/b = 0.55, none of the mixtures were air-entrained. Freeze-thaw testing was initiated after 28 days of curing in water. None of the samples, including those that were air-entrained, had satisfactory air-void systems. The concrete incorporating SF showed small but insignificant increase in the spacing factor with increasing amounts of SF. The test results showed that all mixes with w/b of 0.25 had DFs above 90%, decreasing somewhat with increasing SF content. For higher w/b ratios none of the concretes performed satisfactorily, but the general trend was that the poorest performance was for 20 and 30% SF contents. This is in line with the results obtained by Carette and Malhotra [1983a], which indicated that high (20-30%) SF content at w/b ratios in the range 0.35-0.55 is detrimental to frost resistance, while lower SF contents generally appear to be beneficial over a wide range of w/b ratios.

Pigeon et al. [1986] tested air-entrained and non air-entrained concretes at w/b ratio of 0.5 with and without 10% SF under ASTM C666, Procedure A. The use of SF decreased the internal cracking of the non air-entrained concretes damaged during the tests. The air void system tests indicated that the spacing factor for a given air content was lower in SF concrete than that in PC only concrete, suggesting that the entrained air bubbles are generally smaller with higher specific surface. Scaling was much less severe for the SF concretes, for all values of the spacing factor.

Hooton [1993] tested non air-entrained concretes incorporating SF at replacement levels of 10, 15, 20% at 0.35 w/b ratio; ASTM C666 Procedure A was again adopted. The control mix failed the 60% dynamic modulus criterion at 56 cycles. While the control (PC only) concrete rapidly failed, all of the SF concretes easily survived 900 cycles (three times the normal duration) even though the specimens were not air-entrained, and the spacing factors were above 500 μm. The author suggested that the excellent performance of SF concretes was due to self desiccation obtained from a refined pore structure, combined with low permeability, resulting in less than critical saturation levels. In addition SF concretes were reported to have better scaling resistance than the control concrete.

More recently, Sabir [1997] tested freezing and thawing durability of specimens of air-entrained and non air-entrained concretes with up to 10% SF replacing PC. The tests were carried out in accordance with ASTM C666, Procedure A with one cycle of freezing and thawing per 24 hours. The incorporation of SF led to reduced DFs over those obtained for the control concrete, but after 210 cycles of freezing and thawing, all concretes were rated as frost resistant with DFs higher than 85%. However the SF concrete showed considerably less scaling than the control concrete. Earlier work [Sabir and Kouyiali, 1991] showed similar results. It was then found that concrete incorporating SF by up to 12% and subjected to 35 24h cycles of freezing and thawing, showed somewhat inferior performance when compared with the control concrete. Nevertheless the DFs were all above 95% at the end of the test.

Conclusively the evidence so far suggests that at low w/b ratios (0.25-0.40) and low cement replacement levels (5-15%), SF has a beneficial effect on frost resistance giving smaller reductions in the DFs (>90%) with increasing SF content [Aitcin and Vezina, 1984; Sabir 1997]. Higher SF contents (20-30%) have detrimental effects over a range of w/b ratios of 0.35-0.55 [Carette and Malhotra, 1983a; Yamato et al., 1986, Batrakov, 1992]. It is sometimes stated in technical publications that SF increases the resistance of concrete to freezing and thawing cycles. This belief is usually based on the fact that the deterioration of non air-entrained concrete containing SF due to freezing and thawing cycles is generally lower than that of PC non air-entrained concretes [Gjorv, 1983]. Air entrainment is generally found to be beneficial in SF concrete [Gjorv, 1983; Malhotra, 1984], but there is evidence [Sorensen, 1983, Hooton, 1993] to suggest that it is possible to produce SF concrete that is frost resistant without air entrainment, provided that the w/b ratio is low (0.35) and the SF content is high enough (10% or more). However the majority of investigators [Virtanen, 1983, Malhotra et al., 1986, Yamato et al., 1986, Hammer and Sellevold, 1990] reported poor performance of non air-entrained SF concretes with low w/b ratios and replacement levels of up to 10%. From the majority of the work described the use of SF seems to decrease surface scaling at all replacement levels [Pigeon et al., 1986, Sabir and Kouyiali, 1991, Hooton, 1993, Sabir, 1997]. Most results did not indicate consistent improvements in the spacing factor and the specific surface of the air voids due to the use of SF, nevertheless SF appears to have no detrimental effect on the spacing factor provided an adequate air content (5-7%) is achieved [Pigeon et al., 1989].

The freezing and thawing behaviour of normal w/c ratio (0.4-0.5) concretes containing SF is related to the concrete's pore structure. The finer pores resulting from the use of SF has both a positive and a negative influence. The smaller average size of the capillary pores decreases the total amount of freezable water. In the interior of the concrete, self desiccation is likely to have reduced the water content below the critical level of saturation so that freezing would not cause damage. The fine pore system also makes it difficult for the concrete to become re-saturated after drying. On the other hand, a dense paste with very low permeability does not allow a rapid enough movement of water out of pores subjected to freezing and into an air void. Thus rapid freezing would lead to damage [Khayat and Aitcin, 1992]. For lower w/c ratios (0.25-0.40), the positive effect of the smaller amount of freezable water may become dominant compared to the negative effect of the reduced permeability, which would result in better freeze-thaw performance [Pigeon et al., 1986].

Fly ash concrete

As is the case with all concretes, in general the resistance of FA concrete to damage from freezing and thawing depends on the adequacy of the air void system, the soundness of the aggregate, the degree of hydration, the strength of binding paste, the maturity and the moisture content. When FA is used in concrete special attention must be given to attaining the proper amount of entrained air, which as in the case of other pozzolans, should remain above 5%. In freeze-thaw tests according to ASTM C666, Procedure A on concrete containing FA, Yuan and Cook [1983] showed that the frost resistance of non air-entrained concrete improves with increasing FA content as shown in Figure 2.10(a), although the DF falls below 60% before 150 cycles have been completed. Conversely, air-entrained concrete shows the same frost resistance up to 400 cycles, irrespective of FA content (Figure 2.10(b)). Nevertheless, if comparison is made when the FA concrete has developed adequate strength equal to that of the control (without FA) concrete, no significant differences in freeze-thaw durability have been observed provided the air content remains constant [Larson, 1964, Virtanen, 1983, Dhir et al., 1999]. A minimum strength of 20 N/mm^2 at the time of exposure is suggested in some publications to ensure adequate freeze-thaw resistance [Carette and Malhotra, 1987; Dhir et al, 1999]. This is in agreement with previous work [Roberts and Scheiner, 1981, Kobayashi et al., 1981] where both FA and control concrete showed that increasing compressive strength allowed greater maximum spacing factors for good frost resistance. Furthermore freeze-thaw tests when conducted after long curing periods have indicated that with the incorporation of FA, the resistance to frost attack significantly improves due to the development of strength equal to or greater than that of equivalent PC only concrete. Using ASTM C666 testing procedure, most investigations recommend curing FA concrete for 21 to 28 days to obtain good frost resistance. Very limited data are available using other test methods and Matthews [1989] observed good performance from concretes containing FA cements (28-30%) using the BS 5075 test with w/b ratios of 0.49-0.50 and air contents of 5.5-6.2%.

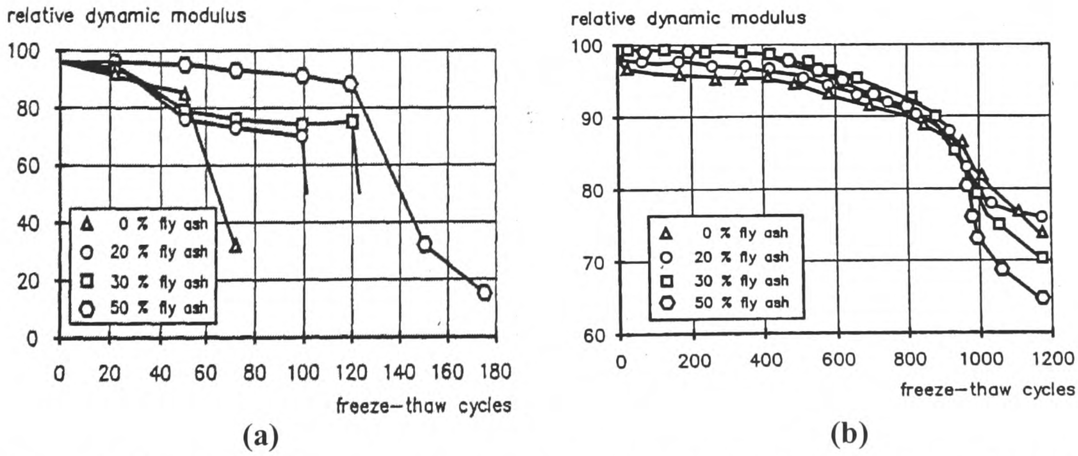


Figure 2.10 Relationship between relative dynamic modulus and number of freeze-thaw cycles for (a) non air-entrained and (b) air-entrained FA concrete [after Yuan and Cook, 1983].

In general the observed effects of FA on the air void system characteristics support the view expressed by Larson [1964] and agreed by many other researchers later on [Rodway, 1988, Dhir et al., 1999] that FA has no apparent ill effects on the air voids in hardened concrete. When a proper volume of air is entrained, characteristics of the void system meet generally accepted criteria. Many other studies [Carette and Malhotra, 1987] have confirmed that the spacing factor is not affected by the presence of FA, provided that the dosage of air entraining admixture is adjusted to achieve the same level of air content. The results obtained for the air void parameters for PC and FA concretes over a range of design strengths (20-50 N/mm^2) and w/b ratios (0.4-0.6) indicated that these changed very little with concrete design strength, although Dhir et al., [1999] noticed slight improvement in FA concrete compared to PC concrete. Dhir et al. [1999] also found that concretes had DFs of around 30% at the 2.5% air content, for both the PC and FA mixes, but the freeze-thaw durability performance improved significantly (in excess of 90%) when the air content was increased to only 3.5%. Thus, it would appear that the air content included in the mix is the main controlling factor of the air void system. Dhir et al. [1999] also clarified that for PC concrete, in general, up to a spacing factor of approximately 500-600 μm, good freeze-thaw durability was obtained (DF > 90%) but for FA concrete, the corresponding range was 400-550 μm. The beneficial effect on spacing factor may be due to the increased admixture dosage level required by FA to achieve the air content, as the air void parameters are thought to be direct functions of the AEA dosage used [Gay, 1986]. Also, the reduced spacing factors required in FA concrete to ensure enhanced freeze-thaw durability may be related to the reduced permeability of FA concrete compared to that of PC concrete, and therefore greater difficulty in water movement and hence pressure relief during periods of freezing in FA concrete [Dhir et al., 1987].

In agreement with Klieger and Gebler [1987], Langan et al. [1990] observed that owing to the initial lower rate of strength gain of FA concrete, coupled with the relatively high replacement levels (> 40%), FA mixtures have a significantly lower strength than the control mixtures at the start of the test and thus less resistance to scaling. Yuan and Cook [1983] observed that when the FA level in air-entrained concrete was increased to 50%, more scaling damage was observed after 400 cycles of freezing and thawing. Sturrup et al. [1983] found that that there was a correlation between surface scaling and carbon content of the FA.

Gebler and Klieger [1986] performed freeze-thaw tests on 75 x 75 x 285 mm prisms on concretes containing different FAs, using Procedure A of ASTM C666. Their study showed that air-entrained concrete with or without FA had good resistance to freezing and thawing in water. The DFs exceeded 98% and weight losses were less than 5%. The expansion measurements showed small changes in length (0.001 to 0.010%). Ouyang and Lane [1996] conducted freeze-thaw tests on concrete cores with 15% of the cement replaced by FA. The w/b was kept constant at 0.43. The freeze-thaw cycling was conducted in accordance with Procedure B of ASTM C666 and continued until the failure of the sample or after reaching 800 cycles. Selected concretes were tested at different ages and cured under different regimes. It was found that irrespective of the curing method and age, concrete with 15% FA showed greater expansion than those of similar mixes without FA. Some of the FA mixes showed as much as 0.25% expansion at the end of the 800 cycles as compared to 0.15% for the control concrete.

Concrete containing FA has been used in many parts of the world for several decades. Various standards and codes have generally limited the use of FA in structural concrete from 10% to 25%. Relatively large volumes of FA are used only in mass concrete. The development of structural concrete utilizing high volumes of FA in recent years initiated many investigations on high volume FA concrete. The investigations confirmed that high volume FA concrete has many excellent properties [Bilodeau et al., 1994]. Studies on the frost resistance of air-entrained high volume FA concretes revealed no significant differences in freeze-thaw performance as compared to PC only concrete of equal strength and equal air content. Lane and Best [1982] came to the same conclusion after conducting freeze-thaw tests on concretes containing 0, 40, 80 percent by weight of cement FA and air contents varying from 8 to 10 percent. Freeze-thaw tests conducted by Joshi et al. [1987], on concrete with 50% cement replaced by FA, exhibited relative dynamic modulus of elasticity values in excess of 60% after 300 cycles. They also reported that FA concrete showed some scaling after 150-200 cycles and exhibited about 2% weight loss at the end of the 300 cycles. Similar results were later reported by Langan et al. [1990] and Joshi et al. [1993].

The influence of FA on the frost durability of concrete, is still in dispute. The contradiction between some of the published results can probably be explained by the slow reaction rate of FA, which means that concretes of different mechanical strengths are often compared. However, the frost resistance of two different concretes with the same mechanical resistance is not expected to be significantly different. This is because the capillary porosity of concretes containing FA, although somewhat higher, is more refined. Schiepl and Hardtle [1994] reported that the main effect of pozzolanic reactions due to FA addition is to change the pore size distribution, the total porosity remaining mostly unchanged. It seems that the use of FA can sometimes modify the rate of deterioration of concretes having an inadequate air void system, but the resistance of properly air-entrained concretes to freezing and thawing is not detrimentally affected by the use of this material.

The phenomenon of pore refinement resulting from pozzolanic reactions leads to the breaking of continuity of the capillary pore structure and the creation of smaller capillary pores. The freezing temperature of water in small capillary pores formed by FA addition is reduced and thus freeze-thaw durability of concrete is improved. With the addition of FA, the water tightness of the paste is also enhanced and thus the rate of water penetration is reduced. This reduction in water ingress rate, together with the decreased freezing temperature of capillary pore water and the reduction of the degree of saturation improves the resistance of FA concrete to frost attack. On the debit side, the reduced permeability of hardened cement paste due to FA addition can retard internal moisture migration through the cement matrix whereby high internal pressure can develop that may cause cracking and deterioration of concrete.

To date the relationships linking the mechanism of frost attack and the microstructure of the cement paste are not well understood. In the study by Schiepl and Hardtle [1994], no clear correlation was found between frost resistance and change in pore structure of concrete caused by FA addition. However, the authors reported that frost resistance to scaling of FA concrete is dependent on the changes to pore structure. FA concrete has been found to exhibit greater surface scaling than PC concrete in many laboratory studies especially those which involve high volume FA replacement levels. Surface scaling is a progressive type of deterioration that slowly eats away very thin layers of paste and mortar and is perhaps the most evident, as well as the most common form of frost damage. Figure 2.11 shows, for three typical concretes, the gradual increase in the mass of scaling debris with the number of freezing and thawing cycles. In the vast majority of cases salts are associated with surface scaling but can also occur when concrete simply freezes in water. Scaling is a much more complex problem than frost induced internal cracking, and the mechanisms of de-icer salt scaling are still today not well understood. However it is accepted that the phenomenon is largely related to the fact that the deterioration affects the very surface layer (or 'skin') of concrete. It is known that these layers are mostly made of cement paste which often tends to be more porous than that of the bulk concrete [Kreijer, 1984].

The influence of pozzolans on the scaling resistance of concrete has been investigated by many researchers. Although some contradictory results are reported in the literature, e.g. Sorensen [1983] and Langlois et al. [1989], numerous other studies have indicated that it is possible to produce scaling resistant concrete if the amount of replacement of PC by SF is kept below 10% of the total mass of binder [Sellevold and Farstad, 1991, Hammer and Sellevold, 1990, Bilodeau and Carette, 1989]. Other laboratory studies have shown that the use of FA in properly air-entrained concretes reduces significantly the scaling resistance of concrete [Gebler and Klieger, 1986, Klieger and Gebler, 1987, Whiting, 1989, Bilodeau et al., 1991, Bilodeau and Malhotra, 1992]. According to most studies, the amount of FA should be limited to approximately 20% of the total mass of binder in order to minimize the concrete's surface scaling.

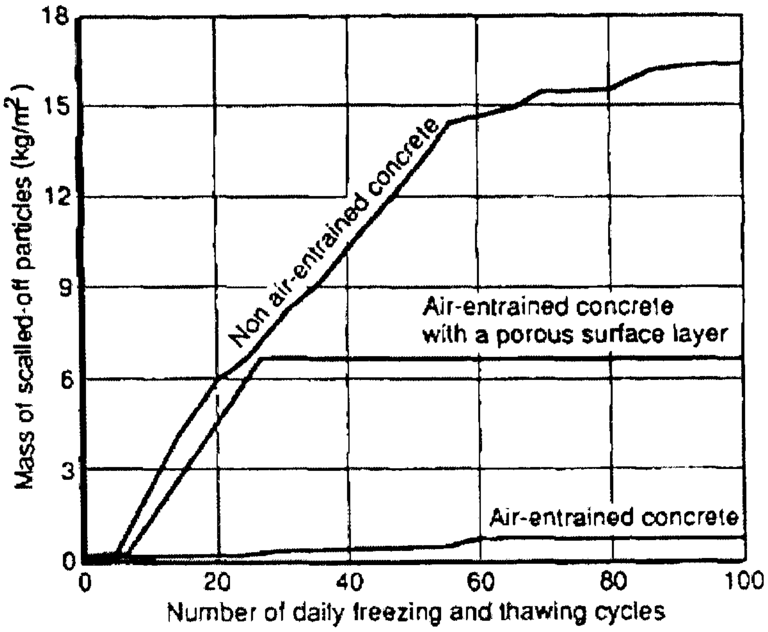


Figure 2.11 Typical relationship between the mass of scaled-off particles and the number of freezing and thawing cycles from three concrete mixtures [after Pigeon et al., 1996].

<u>**MK concrete**</u>

The limited data on freeze-thaw durability of MK concrete support the general view that properly air-entrained concrete gives excellent performance against freezing and thawing under ASTM C666. Zhang and Malhotra [1995] showed that MK and SF concrete at 10% replacement levels with around 6% air content gave similar performance to PC concrete after 300 cycles of freezing and thawing with DFs of about 100%. There were insignificant changes in length, weight, pulse velocity and resonant frequency of the test prisms and no differences between the air void parameters of the PC, SF and MK concretes were obtained. The values of the specific surface were 21.2, 17.9, and 22.2 mm^{-1} for the PC, MK and SF concretes, respectively; the corresponding values of the spacing factor were 0.15, 0.22 and 0.17 mm, respectively. Girodet et al. [1997] examined the freeze-thaw resistance of mortar specimens containing MK as partial PC replacement. As with SF, MK was found to improve the durability of the mortars tested. This was attributed to the pore refinement produced by the pozzolanic activity.

2.4 Porosity, pore size distribution and pozzolans

Generally the key parameters that influence the durability of concrete are the porosity and pore size distribution of the mortar phase of concrete. Porosity is a major component of the microstucture of the hydrated cement paste and influences the compressive strength, permeability, durability and other properties of cement paste. For this reason when investigating the durability performance of concrete containing pozzolans, the measurement of porosity and pore size distribution is essential in order to interpret their performance. Total pore volume and threshold radius are normally taken as indices of the pore structure for comparison of pastes or mortars. However, it is well known that the critical factor affecting the performance and durability of concrete is the pore size distribution, rather than the total porosity. This is because it is possible for two different solid materials with exactly the same pore volume to exhibit completely different physical characteristics depending on the nature of the pore sizes present and their distribution [Winslow, 1989]. Pore structure is a time-dependent property because as the cement hydration progresses, large capillary pore spaces are filled with hydration products, thus refining the size of these pores and at the same time increasing the cumulative volume of very fine gel pores [Hooton, 1986].

According to Klemm and Klemm [1997] the most important range of pore diameters from the point of view of structural damage due to the action of frost is believed to be between 0.3 and 3 μm as the capillary flow takes place mainly in pores having such diameters. Pores having diameters outside this range are thought to affect the capillary flow to a lesser degree. This is attributed to the increased significance of the effects of the surface forces in the case of the smaller diameter pores and gravity forces in the case of the larger diameter pores. Transformation from the liquid to the crystalline state for pores whose sizes are in the above range must cause damage because the ice cannot find an outlet for its expansion. The pore structure of cement paste, and hence the performance under frost action is influenced by whether AEAs are added. For example, using mercury intrusion porosimetry (MIP), Litvan (1983) expressed the view that air-entrained concretes performed better under freeze-thaw conditions because their total pore volume of pores in the range 0.35-2 μm was much higher than for non air-entrained concretes. In agreement with Litvan [1983], Cheng-yi and Feldman [1985] found that replacement of PC in mortars by 10% SF is enough to ensure improved frost resistance, with no need for air entrainment, because of the increase in volumes of pores of sizes ranging from 20 to 2 μm and 0.35 to 2 μm, and to the discontinuity of these pores. Bredy et al. [1989] reported that hydrated blended cement with 30% replacement by MK contained mostly narrow necked pores (< 0.03 μm) and suggested that an improvement in durability under freezing and thawing conditions would be obtained.

Mineral admixtures such as SF, FA and MK influence the pore size and pore size distribution and accordingly durability. With the addition of pozzolanic materials the calcium hydroxide produced by cement hydration reacts with the pozzolan and produces additional C-S-H gel which has a pore blocking effect, further refining the pore structure [Khatib and Wild, 1996]. When, for example, SF is blended with cement, the total porosity of the paste is generally reduced and a finer pore structure, relative to that in PC paste, develops. A paper by Durekovic [1995] on PC-SF pastes of low w/b ratio (0.28) showed that the pore volume decreased systematically with increase in curing time and also generally decreased with increase in SF content. FA, however, appears to be anomalous [Young, 1988] in this respect as PC-FA blends produce (other than at very long curing times) higher porosities and a coarser pore structure than the control paste, even though the permeability was reduced. This is explained in terms of the development of fragile barriers separating large pores which reduce permeability but which are destroyed by the high pressures employed in MIP. Recently Pandey and Sharma [2000] found that the porosity of cement mortar mixed with FA was higher and the pore size distribution was shifted toward larger pores than that of the cement mortar without FA, at ages of 7 and 28 days. However, at 90 days and later, due to the formation of more pozzolanic reaction products, the porosity approached the values of control PC mortar. Frias and Sanchez de Rojas [1997] reported an abnormal behaviour on the evolution of porosity of PC-FA mortars with FA contents between 0% and 40% at 28, 90 and 365 days of curing. For example it was found that at 365 days of curing, in all mortars studied, a bimodal pore size distribution was detected i.e. there were two maxima on the pore size distribution curve, one at 10-12 nm and another at about 100-200 nm. It was also shown that the fineness, particle shape and pozzolanic reaction of the FA play important roles on the development of the pore structure. In a recent study by Khan et al. [2000] cement pastes covering a wide range of FA/SF blending proportions were investigated. The authors found that as FA was introduced in the ternary blended systems the porosity increased and none of the mixtures achieved the porosity of the control (PC only) paste.

The role MK plays in modifying the pore structure has been examined by some investigators. Bredy et al. [1989] reported an increase in the total porosity of PC-MK pastes (relative to pure PC paste) for MK contents in excess of 20% at a curing time of 28 days. From their porosimetry data the authors discounted any collapse of the internal microstructure and attributed the phenomenon to the filler effect of the fine MK particles. Khatib and Wild [1996] reported a refinement of the pore structure and an increase in total intruded pore volume between 14 and 28 days of curing for pastes with 5%, 10% and 15% MK. It was also found that the threshold value and the proportion of large pores (radii > 0.02 μm) of the paste decreased as the MK content in the paste increased. Frias and Cabrera [2000] conducted MIP tests on cement pastes containing 0, 10%, 15%, 20% and 25% MK with a w/b ratio of 0.55 and cured for periods from 1 to 360 days. The authors found that the total porosity of the pastes increases with respect to PC paste at ages above 56 days. Below this age the values showed similar porosities in all pastes. It was suggested that MK had no important effect on the total porosity, probably because of the high w/b ratio used. The best evidence of the influence of MK on the fineness of the pore structure was detected in pores with diameter smaller than 1 μm. It has been also reported [ECC International, 1996] that MK reduces the volume fraction of capillary pores of sizes 0.05-10 μm which is normally associated with increased permeability.

O'Farrell et al., [2001a] reported the results of an investigation on the pore volume, pore size distribution and threshold radius of mortars that contained ground brick which partially replaced PC by 0, 10, 20 and 30% cured for periods of up to one year. It was found that at short curing times increasing ground brick contents in mortar resulted in increased intruded pore volume, reduced percentage of fine pores and increased threshold radius relative to PC mortar. At long curing periods these four parameters approached those of the control mortar.

2.5 Sorptivity, water absorption and pozzolans

Two aspects of the water absorption characteristics of porous construction materials are of particular interest and practical significance. These are the total water absorption and the capillary suction. For example in the use and specification of clay bricks total water absorption is often taken as guide for the prediction of frost resistance, in that bricks of high strength and low porosity have generally proved to be frost resistant in practice. It is generally accepted that the durability of mortar and concrete largely depends on the movement of water and gases through the matrix. For example, the presence of water in concrete can lead to cracks which result from freeze-thaw cycles or the invasion of water in concrete provides a mechanism and path for the penetration of deleterious materials like chlorides and sulfates. Sorptivity characterises the material's ability to absorb and transmit water through it by capillary suction. It is a property of unsaturated materials and it is directly related to durability for above ground structures [Sabir et al., 1998]. It is generally found that water transport in concrete is predominately controlled by the bulk of hardened PC paste, which is the only continuous phase in concrete [Larby, 1993]. Aggregates can also affect the transport properties but these, in general, contain pores which are discontinous and do not allow water movement by capillarity, and hence do not contribute to sorptivity.

It should be noted that the total water absorption represents the total evaporable water content of specimens which have been dried at 105°C for 24 hours whereas sorptivity represents a suction rate by which capillary pores (in specimens which have been dried to constant weight at 40°C) take up water. These two parameters therefore represent different material characteristics. As sorptivity is a function of capillarity it is much more dependent on pore structure (especially pore size) as opposed to total open porosity which is of importance in water absorption. For specimens with identical pore structures and pore size distributions one would expect sorptivity to increase with increase in total absorption. However for specimens of differing pore structures and pore size distributions it is quite possible for sorptivity to increase whilst total absorption decreases.

It is generally accepted [Parrot, 1992, Martys and Ferraris, 1997] that the water absorption of concrete is reduced as the duration of moist curing increases. Parrot [1992] observed that the influence of moist curing time on the rate of water absorption of PC concrete is very small beyond 3 days. However if the PC in the concrete is partially replaced by pozzolans (i.e. 30% FA) absorption rates are initially much greater but continue to fall significantly with increased specimen curing time up to at least 28 days.

The presence of mineral admixtures, such as FA and SF in a cementitious composite has the effect of reducing sorptivity values due to the formation of finer, more tortuous capillaries, as a result of enhanced C-S-H gel formation arising from the pozzolanic reaction [Gopolan, 1996, Marchese and D'Amore, 1990]. Durekovic [1995] observed a marked decrease in capillary water suction at early ages (1 day) with increase in SF content for water-cured PC-SF pastes. However, some researchers [Ho and Lewis,1987, Gopolan 1995] observed that the sorptivity of FA concretes when compared with PC concretes of similar strength was marginally higher. In a recent study Sabir et al. [1998] carried out sorptivity and total water absorption measurements on mortar samples in which the PC was partially replaced by 10, 20 and 30% ground clay brick from different sources. The authors found that the control mortar exhibited greater resistance to water absorption by capillary suction than the mortars containing ground brick, the sorptivities of which increased with increasing level of PC replacement by ground brick. However, with increasing curing time the sorptivities of ground brick mortar decreased, and at 90 days and for certain replacement levels some mortars exhibited sorptivities below that of the control mortar. The above behaviour confirmed previous reports by the authors [Wild et al., 1997], of the pozzolanic effect of ground brick which produces pore refinement at extended curing times, but is not manifested at the early ages when the ground brick imparts increased porosity to the mortar. Similar behaviours were observed for total water absorption measurements indicating that ground brick alters the matrix structure with respect to both total porosity and interconnected capillary pores in similar ways at all ages. Similar observations for sorptivity and total water absorption of mortar incorporating waste clay brick from the same sources were made by O'Farrell et al. [2001b].

Sorptivity is largely affected by the curing conditions, especially in the case of FA concrete. Gopolan [1996] found that when fog cured concretes of the same strength were considered, the sorptivity of the FA concrete was lower than that of the PC concrete, while under dry curing the FA concrete showed higher sorptivity than PC concrete. Kelham [1988] also demonstrated that replacement of PC with 25% FA produces substantially lower sorptivity relative to the PC (control) concrete in water cured samples but higher sorptivity relative to the control concrete in air cured samples. Bentur and Jaegermann, [1991] pointed out that the detrimental effect of inadequate curing on the absorption properties of the outer zone of concrete is becoming greater as the FA content increases. The influence of the composition of PC-FA-MK binders on sorptivity of concrete cured both in air and in water was reported by Bai et al. [2001]. It was found that increasing the MK content of the water cured PC-FA-MK concrete reduces the sorptivity to values below that of the control whereas the sorptivities of PC-FA concrete exceeded that of the control. On the other hand air cured concrete showed higher sorptivity than equivalent water cured concrete and the difference was substantial both for PC concrete and PC-FA concrete. In contrast, for PC-FA-MK concrete, the difference was reduced as the MK content was increased, such that at high MK levels the air cured and water cured concrete sorptivities were similar. This is explained by the fact that when MK is present a much finer pore structure rapidly develops preventing surface evaporation in air cured concrete thus allowing hydration in the surface layers to continue unabated.

Other important factors that influence sorptivity are the sample location within concrete and the method of drying of the sample. Khatib and Mangat [1995] have shown that the sorptivity values determined on samples taken from the top surface of a concrete cube can be several times greater than those for concrete taken from the bottom surface of the cube. Also the common method of oven drying at 105°C [Gopalan, 1996, Kelham, 1988] can cause internal shrinkage and microcracking and subsequently will result in artificially high sorptivity values. When concretes incorporating different pozzolans are compared the method of drying could be of critical importance since different pozzolans could behave differently in a given drying regime. For this reason other workers [Sabir et al., 1998, Hall, 1989] have used a more 'gentle' method of drying to constant weight at 40°C.

Chapter 3 – Materials and experimental investigation

The experimental investigation described in this thesis is divided into two separate studies. In the first several concrete mixtures were prepared to investigate the roles played by superplasticizer and air entraining agent on the properties of the fresh concrete, i.e. workability and air content. In this part of the investigation samples were also prepared to evaluate the compressive strength development and to establish the relationship between compressive strength and air content.

The second study deals with a detailed examination of the freeze-thaw performance of concretes employing various amounts of pozzolans as partial replacements for PC in the control (PC only) concrete. The pozzolans employed were fly ash, silica fume and metakaolin. Several binder (PC + pozzolan) compositions for both binary and ternary blends were considered. This investigation involved preparation of prism samples for freeze-thaw testing in accordance with Procedure A of ASTM C666-97 [1997] and BS 5075: Part 2 [1982]. Because of restrictions imposed by the freeze-thaw equipment on the total volume of concrete being tested at any one time, it was not possible to provide the rate of freezing and thawing required by ASTM C666-97. The work conducted in the present study involved testing various concretes subjected to either one or two cycles of freezing and thawing per 24 hours. This was considered reasonable, as the main aim of the present investigation is to compare the performance of concretes of various pozzolanic compositions and not to obtain an indication of performance in the field. Furthermore, it is often a criticism that the ASTM test procedure is too severe. The freeze-thaw tests were supplemented with detailed microscopic examinations of polished sections of concrete to determine the air-void characteristics.

Data on sorptivity, water absorption and mercury intrusion porosimetry were collected from samples of the concretes under investigation. These data give further *information on the matrix structure of the concretes examined. This chapter gives details of the materials employed, mixture compositions and experimental procedures adopted in the study.*

3.1 Materials

Cementitious materials

The cement used throughout this part of the investigation, was class 42.5 N Portland cement (PC) complying with the requirements of BS 12 [1991]. The SF was supplied by Elkem Materials Ltd in a slurry form composed of a mass ratio of SF solids to water of 1:1. Silica fume is a by-product resulting from the reduction of high-purity quartz with coal in an electric arc furnace during the production of silicon metal or ferrosilicon alloys. In the process SiO vapours are produced which oxidize and condense in the form of very tiny spheres of non-crystaline silica (0.1 μm average diameter). The product, which is highly pozzolanic, is recovered by passing the outgoing flue gas through a baghouse filter. Due to the extremely fine particle size and low bulk density of SF, the handling and transportation is generally carried out with material in the form of a slurry or a pelletized product. MK was supplied by Imerys (formely ECC International). MK is a processed ultrafine pozzolan produced by calcination of a high-purity kaolinite clay at temperatures between 700-800°C. The product is pulverized to a very fine particle size (average 1-2 μm) to make it highly pozzolanic. The FA, which was supplied by Ash Resources Ltd, is the ash precipitated from the exhaust gases of coal-fired power stations. FA is made up of very fine, predominately spherical glassy particles (which is advantageous from the water requirement point of view) and have a very high fineness: the particle sizes range from less than 1μm to over 100 μm.

Details of the physical and chemical properties of the PC and pozzolans used are given in Table 3.1. The principal reactive component in pozzolans used for the partial replacement of cement is amorphous silica. MK resembles SF in some respects, particularly in terms of its very high specific surface (> 12000 m^2/kg) and also that it is a silica based product, which on reaction with CH produces C-S-H gel.

However, as shown in Table 3.1, unlike SF which comprises principally amorphous silica (85-98%), MK has a high alumina content (41%), which on reaction leads to formation of alumina based hydrates, in addition to the C-S-H gel. The chemical composition of FA is also dominated by silica, and alumina. In this case the amorphous silica occurs as alumino-silica glass and it is the glass that is the active component of FA. The glass content is normally in the range 71-88% [Helmuth, 1987].

Table 3.1 Properties of PC, SF, FA and MK used in the study.

Property	*PC*	*SF*	*FA*	*MK*
Oxide composition: %				
SiO_2	20.00	85-98	49.8	52.1
Al_2O_3	4.30	1.5	26.4	41.0
Fe_2O_3	2.30	3.0	9.3	4.32
CaO	64.00	0.7	1.4	0.07
MgO	2.20	2.0	1.4	0.19
SO_3	3.00	-	0.8	-
Na_2O	0.16	1.0	1.5	0.26
K_2O	-	3.0	3.5	0.63
TiO_2	-	-	1.0	0.81
Cl	-	-	0.01	-
C	-	3.0	-	-
LOI	2.80		4.9	0.6
Mineral composition:%				
C_3S	61.7			
C_2S	11.4			
C_3A	7.6			
C_4AF	6.8			
Physical properties:				
Colour	Grey	Grey	Black	White
Specific gravity	3.08-3.14	1.40	2.30	2.5
Bulk density: kg/m^3	1000-1450	200-300	1000	300
Specific surface: m^2/kg	346	15000-30000	547	14130

Pozzolans like FA, SF and MK mainly derive their CH reactivity from the combination of two factors, namely the non-crystalline structure and high specific surface. The specific surface of FA is usually 250-600 m^2/kg as determined by the Blaine air permeability method. The high specific surface of FA means that the material is readily available for reaction with CH. However the specific surface of FA is not as high as those of MK or SF which means partial replacement of PC by ultrafine pozzolans like SF and MK is much more effective in enhancing concrete properties than replacement by FA, particularly at early stages of curing.

The particle size distribution plots obtained by the author for PC, FA and MK used in the work are presented in Figure 3.1. The plots were obtained using a Malvern Instruments Mastersizer 2000 unit with a Scirocco dry feed unit. The author was unable to obtain the particle size distribution of the SF using lazer analysis due to the agglomaration of the very fine particles of the SF. For comparison reasons a typical particle size distribution of SF reproduced from Mehta [1983] was used instead.

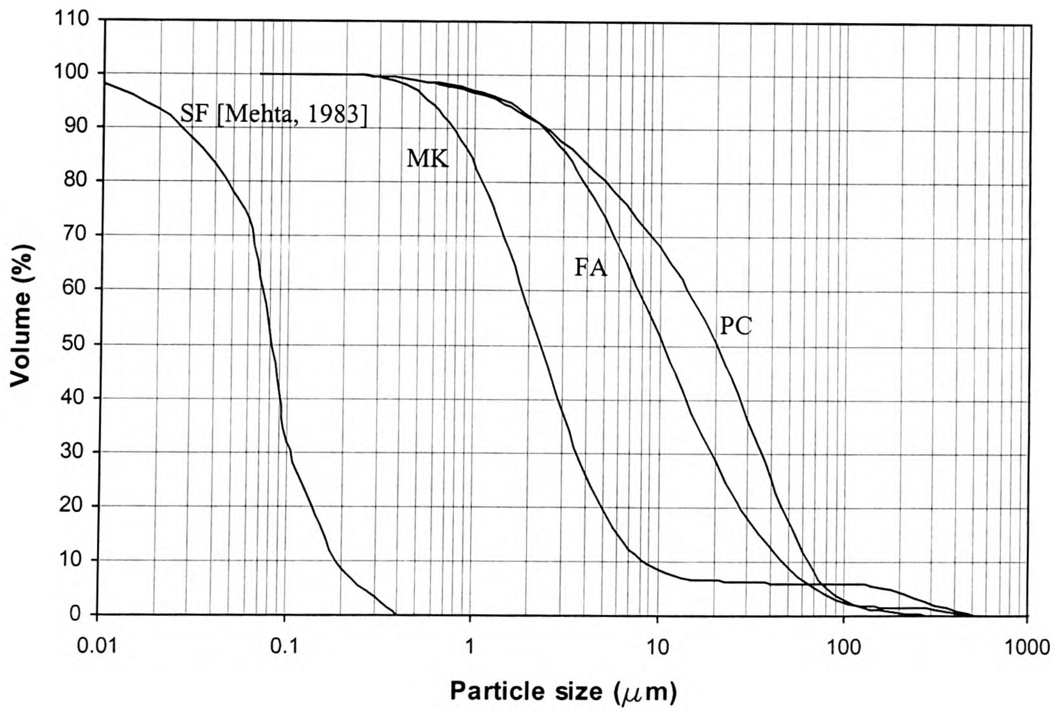


Figure 3.1 Particle size distribution of the PC, MK, FA used in the investigation and typical size distribution of SF reproduced from Mehta [1983].

It can be seen that the size distribution of pozzolans was shifted towards smaller particle sizes as compared to PC. As might be expected SF shows the finer size distribution, followed by MK and FA. It should also be noted that the MK particles are not equidimensional but are flaky, therefore the technique probably overestimates the particle size.

Aggregates

The fine aggregate was natural sea-dredged sand from the Bristol Channel. The sieve analysis performed in accordance with BS 812: Section 103.1 [1985] showed that the sand complied with grades C and M of BS 882 [1992]. The coarse aggregates employed were 10mm maximum size crushed limestone supplied by a local quarry. The gradings of fine and coarse aggregates are shown in Table 3.2.

Table 3.2 Grading of fine and coarse aggregates.

Coarse aggregate		*Fine aggregate*	
Sieve size (mm)	*% retained*	*Sieve size (mm)*	*% retained*
10	1.4	5	10.7
5	98.5	2.36	28.3
2.36	99.6	1.18	36.2
		600μm	45.1
		300μm	84.6
		150μm	99.3

Chemical Admixtures

Trial mixtures were prepared for a range of pozzolanic additions with a commonly employed high range water reducing admixture (Daracem SP1) and the air-entraining agent (Darex AE3). Difficulties were encountered in establishing appropriate dosages of these two admixtures to obtain stable and consistent concrete for the planned range of pozzolanic additions and target air content. In particular it was found difficult to obtain appropriate slumps in the case of the mixtures containing high proportions of SF and MK (15-20%). A more comprehensive range of concrete mixtures was found to be achievable using a more recently developed water reducing admixture, i.e. "Adva Flow" and this was therefore used in subsequent mixtures. Adva Flow (AF) is a synthetic carboxylated polymer based clear liquid superlasticizer complying with BS 5075: Part 3 [1982]. Darex AE3, is a pale yellow liquid air entraining agent, which conforms to the requirements of BS 5075: Part 2 [1982] for air entraining admixtures and is based on the salt of an ether sulphate. Table 3.3 gives descriptions of the Adva Flow and Daracem SP1 water reducing and Darex AE3 air entraining admixtures employed in the current investigation. AF was found to be a much more effective and stable admixture when used in combination with the air entraining agent. Careful control, however, was found to be crucial as slight alterations in the dosages of the superplasticizer can cause very significant changes in workability.

Table 3.3 Properties of chemical admixtures used in the study.

Admixture	*Description/technical information from manufacturers*
Daracem SP1 (superplasticizer)	Based on the salt of a polymeric naphthalene sulphonate. Supplied as dark brown liquid. Specific gravity = 1.19 at 20°C. Recommended addition rate: 500ml-1500ml per 100kg of cement
Adva Flow (AF) (superplasticizer)	Synthetic Carboxylated polymer. Supplied as a clear liquid. Specific gravity = 1.06 at 20°C. Recommended addition rate: 200ml-1000ml per 100kg of cement.
Darex AE3 (air entraining agent)	Based on the salt of an ether sulphate. Supplied as a pale yellow liquid. Specific gravity = 1.005 at 20°C. Recommended addition rate: 60ml-400ml per 100kg of cement.

3.2 Mixture compositions

The water/binder ratio is based on the total cementitious materials, i.e. PC + pozzolans used. In calculating the w/b ratio for the mixtures containing SF, allowance was made for the water included in the slurry. The superplasticizer and air entraining admixture are expressed as percentages of the mass of the binder. All the mixtures were in the proportions of binder: sand: 10mm aggregate of 1: 1.6: 3.1. The binder compositions for the mixtures were calculated on the basis of a constant mass of binder.

3.3 Tests on properties of fresh concrete

The mixtures considered in this study had a binder content of 380 kg/m^3 and a w/b ratio of 0.45. Several preliminary tests were carried out for concretes containing PC only with the two different types of superplasticizers (SP1 and AF) containing the AE3 air-entraining agent. This enabled the admixture performance in the fresh concrete to be examined and the selection of a suitable superplasticizer (AF) to be made. The preliminary tests were performed to obtain the correct material proportions and binder content of the mixtures and establish the range of admixture dosages necessary to give the desired properties. For example it was found that for SF and MK mixtures 0.5% water reducing admixture is needed instead of 0.3% for the control and FA mixtures, in order to maintain appropriate and similar levels of workability. Furthermore the preliminary tests acted as a guide for the development of an appropriate mixing procedure. Details of these preliminary mixtures are given in Table 3.4.

Table 3.4 Preliminary tests for the development of the control mixture.

Mixture proportions					*Admixtures/b (%)*				
PC	*Sand*	*10mm*	*binder b (kg/m^3)*	*w/b*	*SP1*	*AF*	*AE3*	*Slump (mm)*	*Air content (%)*
1	2	3	330	0.45	0.5	-	-	0	
1	1.2	3.5	330	0.45	0.5	-	0.06	collapsed	
1	1.2	3.5	380	0.45	0.5	-	0.12	0	
1	1.4	3.3	380	0.45	0.5	-	0.12	0	3.5
1	1.4	3.3	380	0.45	-	0.20	0.12	collapsed	9.5
1	1.4	3.3	380	0.45	-	0.20	0.06	collapsed	7.0
1	1.6	3.1	380	0.45	-	0.20	0.06	150	6.5
1	1.6	3.1	380	0.45	-	0.12	0.05	40	4.5
1	1.6	3.1	380	0.45	-	0.16	0.06	65	5.0
1	1.6	3.1	380	0.45	-	0.18	0.06	40	4.5
1	1.6	3.1	380	0.45	-	0.20	0.06	60	4.5
1	1.6	3.1	380	0.45	-	0.30	0.06	85	5.0

In addition to the control (PC only) mixtures, mixtures were prepared with 10 and 20% replacement (by mass) of PC with SF or MK, and 20, 30 and 40% replacement of PC with FA. The same total replacement levels (20, 30 and 40%) were employed for the ternary blends of PC+FA+MK mixtures. Each of the three replacement levels contained ratios of FA/MK of 3:1 and 1:1. The proportions for the mixtures employed in this study are given in Table 3.5.

Table 3.5 Mixture proportions, w/b = 0.45, b = 380 kg/m^3.

Concrete	binder (%)				Concrete mixture proportions (kg/m^3)					
					binder				Aggregate	
	PC	SF	FA	MK	PC	SF	FA	MK	Sand	10mm
Control	100	-	-	-	380	-	-	-	663.1	1284.8
PC+SF	95	5	-	-	361	19	-	-	660.7	1280.1
	90	10	-	-	342	38	-	-	658.2	1275.4
	85	15	-	-	323	57	-	-	655.8	1270.7
	80	20	-	-	304	76	-	-	653.4	1265.9
PC+MK	95	-	-	5	361	-	-	19	661.6	1281.9
	90	-	-	10	342	-	-	38	660.1	1279.0
	85	-	-	15	323	-	-	57	658.7	1276.1
	80	-	-	20	304	-	-	76	657.2	1273.2
PC+FA	80	-	20	-	304	-	76	-	655.3	1269.7
	70	-	30	-	266	-	114	-	651.4	1262.1
	60	-	40	-	228	-	152	-	647.5	1254.5
PC+FA+MK	80	-	20	-	304	-	76	-	655.3	1269.7
		-	15	5	304	-	57	19	655.8	1270.6
		-	10	10	304	-	38	38	656.2	1271.5
	70	-	30	-	266	-	114	-	651.4	1262.1
		-	22.5	7.5	266	-	85.5	28.5	652.1	1263.5
		-	15	15	266	-	57	57	652.8	1264.8
	60	-	40	-	228	-	152	-	647.5	1254.6
		-	30	10	228	-	114	38	648.4	1256.3
		-	20	20	228	-	76	76	649.3	1258.1

Mixing was performed in a rotary pan mixer in a room with an ambient temperature of 20 ± 5°C and relative humidity > 50% in compliance with BS 1881: Part125 [1983]. The PC, FA and/or MK were blended together by hand until a uniform colour was achieved. First the aggregates were placed and spread evenly in the pan. One third of the prescribed amount of water was then added to the pan and the mixer was operated for 30s. The contents were kept covered in the pan to avoid loss of water by evaporation. After one minute the blend was added and spread in an even layer over the aggregates. Mixing was re-commenced and continued for 30s. Another third of the mixing water was thoroughly mixed with the air-entraining agent added to the pan and mixing was then continued for an additional minute. Any material adhering to the mixer blades was then scraped off into the pan. Finally the superplasticiser was mixed with the remaining third of water, and added to the pan for a further one minute mixing. A slight modification was made to the above mixing procedure in the case of PC-SF concrete because of the water in the slurry. In this case the second third of water was halved. One half was blended with the SF slurry and added to the pan. The other half was mixed with the air-entraining agent and added to the ingredients in the pan followed by one minute of mixing. This mixing procedure was adopted throughout.

For each replacement level of the various pozzolanic materials used, several dosages of air entraining agent were used to achieve a comprehensive assessment of its effects on the slump, compacting factor and air content of the fresh concrete. The slump, compacting factor and air content tests were performed in accordance with BS 1881: Parts 102, 103 and 106 [1983] respectively. The air content measurements were carried out within 15 minutes of mixing, following the slump and compacting factor tests. A schematic illustration of the air meter used is shown in Figure 3.2. As frost resistance is also dependent on the strength of the concrete, twelve 100 mm cubes; three for each of the curing ages of 7,14,28 and 90 days, were prepared for compressive strength tests. Compaction of the compressive strength test specimens was accomplished using a vibration table. All the test samples were kept in their steel moulds, covered with cling film, for 24 hours and then demoulded and cured in water at 20°C until they were tested.

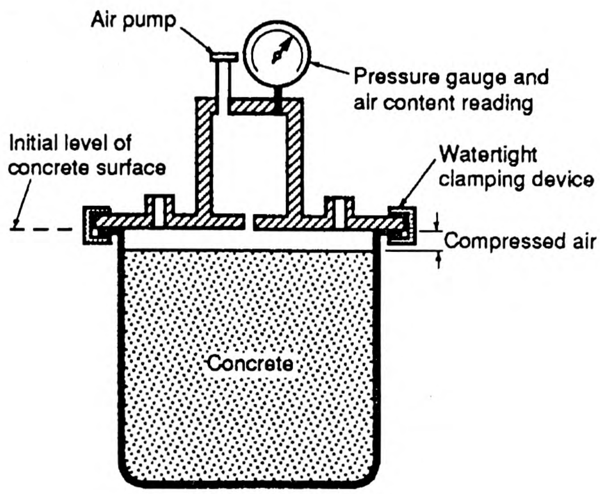


Figure 3.2 Schematic description of the air content meter used for determination of air content of fresh concrete.

3.4 Investigations on concrete in the hardened state

This section gives details of the mixtures employed in the freeze-thaw tests. The concretes examined contained several compositions of the various pozzolans used in this study, i.e. SF, FA and MK.

3.4.1 Mixture proportions

The mixture proportions for the concrete mixtures chosen for the assessment of freeze-thaw durability and microstructural examination of concrete are given in Table 3.6. The w/b ratio and binder content were kept constant at 0.65 and 285 kg/m^3 respectively. In addition to the control (PC only) mixtures, 2.5%, 7.5% and 10% replacement of cement by mass was adopted for mixtures incorporating MK, whereas two replacement levels of 10 and 30% by mass were employed for those incorporating FA. The same total replacement levels (10 and 30%) were employed for the combination of FA+MK mixtures. Each of the two replacement levels contained a ratio of FA/MK of 3:1. The fresh concrete was subjected to slump and air content tests in accordance with BS 1881: Part 102 [1983] and BS 1881: Part 106 [1983], respectively. From each concrete mixture two 75 x 75 x 250 mm long prisms for freeze-thaw testing and fourteen 100 mm cubes were prepared. Twelve cubes were tested for compressive strength and the two remaining cubes were used for sorptivity and water absorption tests and microscopic examinations.

Table 3.6 Mixture proportions, w/b = 0.65, b = 285 kg/m^3.

Mixture	*binder (%)*				*Concrete mixture proportions (kg/m^3)*					
					binder				*Aggregate*	
	PC	*SF*	*FA*	*MK*	*PC*	*SF*	*FA*	*MK*	*Sand*	*10mm*
Control	100	-	-	-	285	-	-	-	678.0	1313.7
PC+SF	90.0	10	-	-	256.5	28.5	-	-	674.4	1306.6
PC+MK	97.5	-	-	2.5	277.9	-	-	7.1	677.5	1312.6
	92.5	-	-	7.5	263.6	-	-	21.4	676.4	1310.4
	90.0	-	-	10	256.5	-	-	28.5	675.8	1309.4
PC+FA	90.0	-	10	-	256.5	-	28.5	-	675.1	1308.0
	70.0	-	30	-	199.5	-	85.5	-	669.2	1296.7
PC+FA +MK	90.0	-	7.5	2.5	256.5	-	21.4	7.1	675.3	1308.4
	70.0	-	22.5	7.5	199.5	-	64.1	21.4	669.8	1297.7

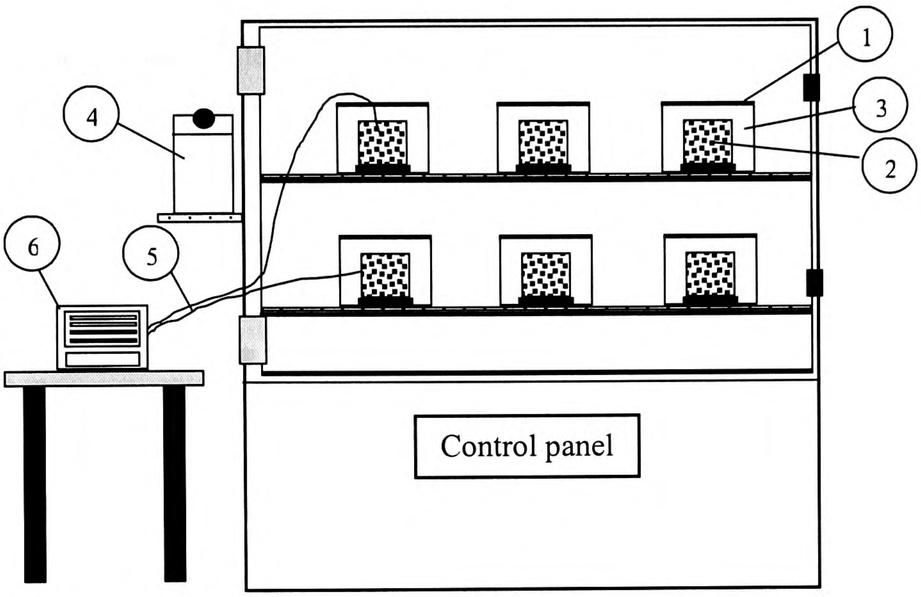
3.4.2 Compressive strength testing

The compressive strength testing was conducted at curing ages of 7, 14, 21 and 28 days, in compliance with BS 1881: Part 108 [1983]. The concrete was compacted in three layers, using a vibrating table. After compaction, clingfilm was placed on the finished surface of the cubes to prevent any moisture loss during hardening. Twenty-four hours after mixing, the cubes were demoulded and placed in water at 20 ± 2°C for curing. The concrete cubes were tested in compression on an Avery-Denison compression testing machine with a loading rate of 180 kN/min. Each reported value of compressive strength was the average of three measured values.

3.4.3 Freeze thaw testing

The freeze-thaw testing reported in this investigation was conducted using the procedures described in BS 5075: Part 2 [1982] and ASTM C666-97 [1997]. The BS method is designed to provide acceptance tests for admixtures to meet requirements with regards to air-entrainment for performance under the actions of freezing and thawing. It also deals with the effects of entrained air on the compressive strength of concrete and the action of repeated freezing and thawing under wet conditions. Freeze thaw performance is assessed by measurement of change in length, which is, according to the standard, judged to be the most sensitive and convenient method. The procedure described in ASTM C666 is intended to determine the effects of different formulations and conditioning of concrete on its resistance to the actions of freezing and thawing. It uses the change in the dynamic modulus of elasticity as the principal measurement indicating the extent of internal damage caused. It also recommends the measurements of changes in pulse velocity, weight and the change in length as an optional requirement. Neither standard is intended to provide a quantitative measure of the length of service that may be expected from a specific type of concrete. Both standards recommend tests to be performed on prism samples of similar sizes. Whilst the BS method suggests one freezing and thawing cycle per 24 hours, the ASTM standard recommends a more accelerated exposure of six-twelve cycles per 24 hours. The ASTM requirement is generally regarded as a too severe method of testing. In this investigation the test specimens were initially subjected to one cycle per 24 hours, in accordance with the BS method, and later a somewhat more accelerated cycling of freezing and thawing was used, determined by the limits of the test chamber in relation to the number of specimens tested at any one time. The freeze-thaw testing was performed in a Prior Clave LCH/600/25 model 0.7 m^3 volume capacity chamber. The apparatus consisted of a refrigerating and heating unit, which produces continuous freeze thaw cycles with chamber temperatures in the range of ± 20°C. Figure 3.3 shows a schematic illustration of the freeze-thaw apparatus and the arrangement of specimens in it.

The specimens for freeze-thaw testing were 75 x 75 x 250 mm long prisms cast in steel moulds in accordance with BS 1881: Part 109 [1983]. The moulds were constructed so that cylindrical, stainless steel inserts could be secured centrally in each end face of the prisms prior to casting. The moulds consisted of three compartments so that three prisms could be prepared simultaneously. Using the equipment described above it was possible to house twelve samples at any one time with a capability of producing approximately two cycles of freezing and thawing per 24 hours.



1-Polythene cover
2-Concrete specimen
3-Galvanized steel container filled with water
4-Water tank
5-Thermocouples
6-Temperature recording

Figure 3.3 Schematic description of the arrangement for the freezing and thawing test.

For each concrete mixture two prism specimens were cast. One, without inserts at the ends, was used for the measurements of the dynamic modulus and pulse velocity required by ASTM C666 (Procedure A, freezing and thawing in water), while the other, with inserts, was used for length change measurements in accordance with BS 5075: Part 2 [1982]. Similar to the preparation of the 100 mm cubes for compressive strength testing, the concrete was compacted in three layers using a vibrating table and covered with clingfilm for prevention of any moisture loss during hardening. Twenty-four hours after casting the concrete prisms were demoulded. Once the screws securing the inserts had been removed, the mould was dismantled and the concrete prisms were labelled as to their pozzolan composition and air entrainment status (whether air-entrained or non air-entrained). The prisms were then cured in water for 21 days before being subjected to freezing and thawing.

The two prisms from each concrete mixture were placed in the same galvanized steel container. The containers were labelled with numbers from one to six to enable further identification of the different mixtures. The specimens were surrounded by water at all times while in the freeze-thaw apparatus. This was achieved by supporting the specimens in the containers on perspex bars. Immediately after the specified curing period and at regular intervals thereafter, length change measurements at the centre line of the concrete specimen, fundamental resonant frequency measurements in accordance with BS 1881: Part 209 [1990], pulse velocity measurements in compliance with BS 1881: Part 203 [1986] and weight change measurements were carried out. Length and weight measurements were taken on a surface dry basis. Figures 3.4 to 3.6 show the apparatus used for fundamental frequency, length, and pulse velocity measurements, respectively. When no more resonant frequency measurements could be taken they were deemed to have failed but freezing and thawing was continued with weight loss and length measurements being taken until the prism disintegrated. In other cases the freezing and thawing cycles were continued up to the completion of 120 cycles or more where that was considered necessary. After completion of the freeze-thaw tests the prisms were tested for flexural strength in accordance with BS 1881: Part 118 [1983]. The prism portions were then tested for equivalent cube strength in accordance with BS 1881: Part 119 [1983].

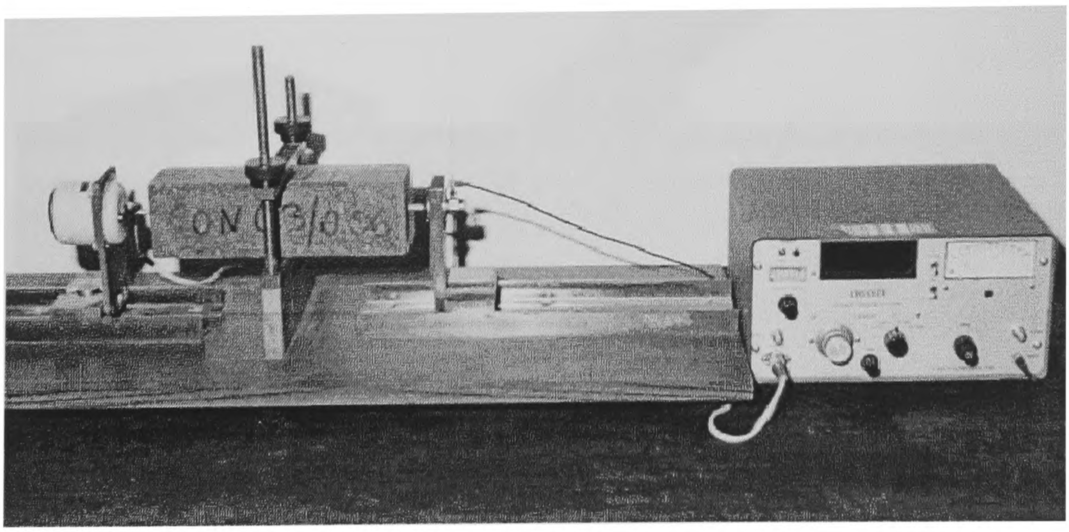


Figure 3.4 The resonant frequency testing arrangement.

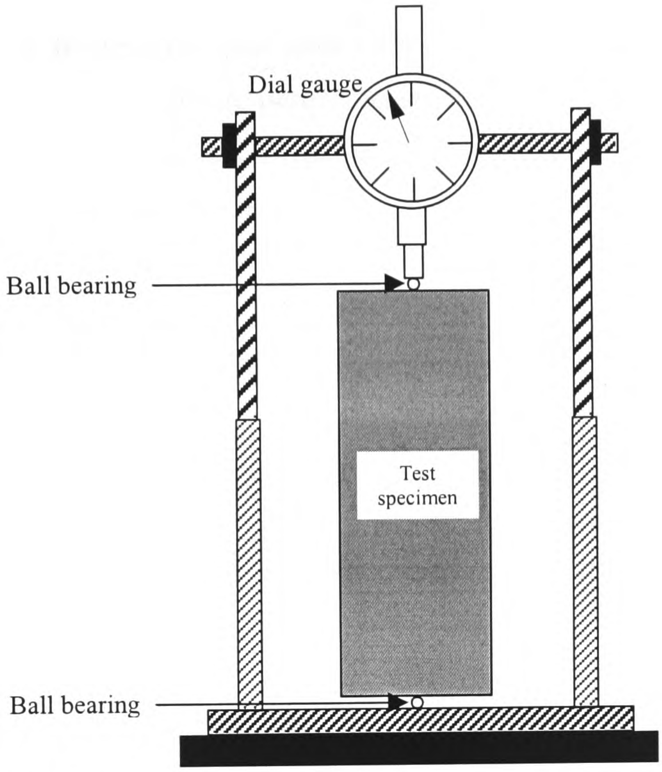


Figure 3.5 Schematic view of the extensometer used to determine length change of concrete prisms.

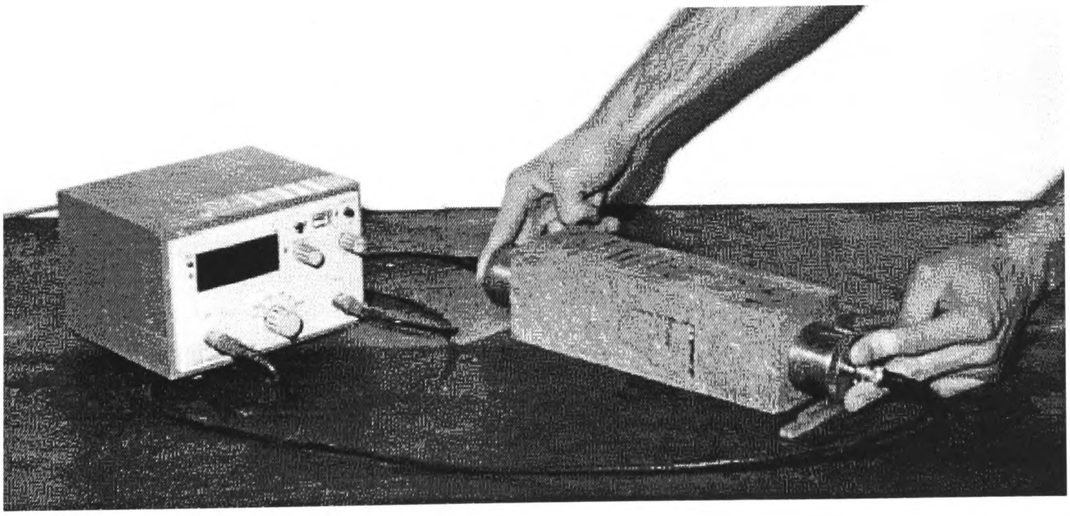


Figure 3.6 Testing arrangement for determination of pulse velocity.

3.4.4 Air void system characteristics

Preparation of the concrete specimens for microscopic examination consisted of first cutting four slices of concrete perpendicular to the finished surface of the cube, of initial dimensions of 70 x 70 x 10 mm as shown in Figure 3.7. The external face slice was then discarded and the remaining slices were reduced to 70 x 35 x 10 mm, because of restrictions set by the size of the microscope stage. Prior to the microscopic examination, each concrete surface was very carefully polished using successively finer silicon-carbide abrasives over a rotating steel plate in order to obtain a plain surface on which the air boundaries of the air voids and of the aggregate particles are sharp and easily discernible.

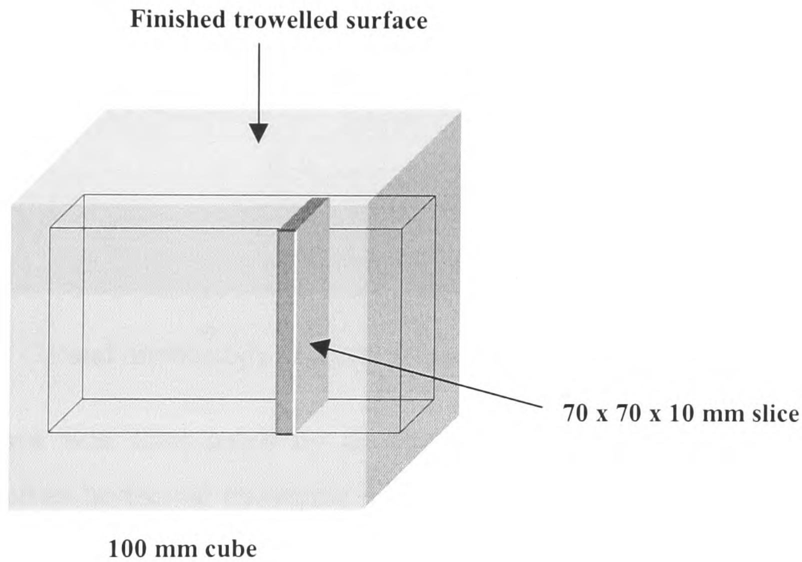


Figure 3.7 Slices 70 x 70 x 10 mm cut from 100mm cube to be used for microscopic examination.

The air void characteristics determined were the air content, the specific surface, the paste content, the number of voids per mm and the spacing factor. The method used in this study was the modified point count method in accordance with ASTM C457-90 [1990]. The optical microscopy analysis set up, developed for this investigation, is shown in Figure 3.8. The 70 x 35 x 10 mm concrete specimen was placed on a point-counter travelling stage moving along two orthogonal directions. The optical microscope was operated over the moving stage at a magnification of 40x. The

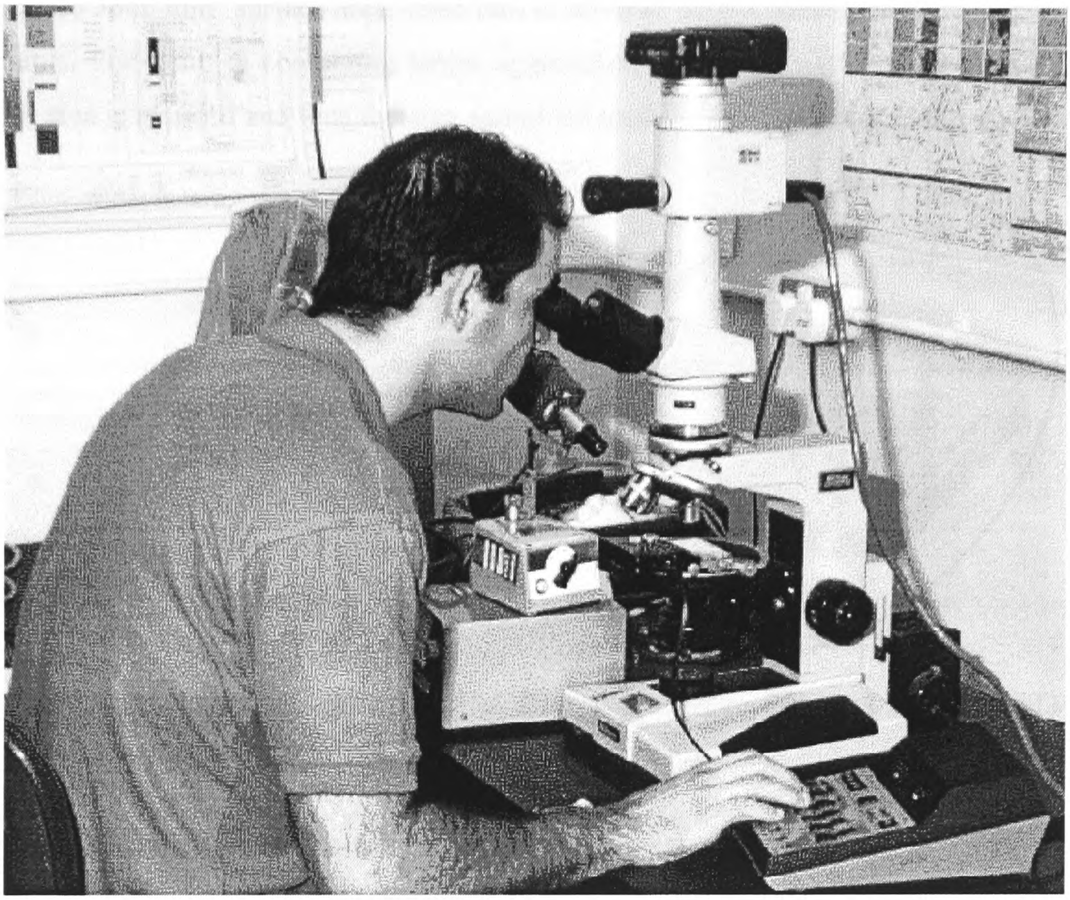


Figure 3.8 Optical microscopy analysis set up.

concrete surface was illuminated by an external halogen spotlight source. The technique involves horizontal traversing of a prepared concrete surface, noting the number of stops, the frequency of voids between stops, and the number of voids and paste met at stops. More specifically the method consists of following with the cross-hairs of the microscope a given number of regularly spaced lines of traverse distributed over the entire surface of the specimen. Due to restrictions on the movement of the point counter stage, the middle area of each specimen was covered and was limited to 24 mm by 14.4 mm as shown in Figure 3.9. For these reasons twenty such areas were examined for each concrete mixture to meet the requirements set up by the standard. In order to provide sufficient precision the ASTM C457 Standard defines minimum requirements concerning the area of the surface covered by the examination, the total length of the lines of traverse and the number of point counts. For the 10 mm aggregate used in this investigation the requirements were to provide 5800 mm^2 surface area, 1905 mm in traverse length and a total of 1125 point counts. For samples containing larger aggregates, the quantity of cement paste per unit area is reduced and thus the area examined must be correspondingly increased.

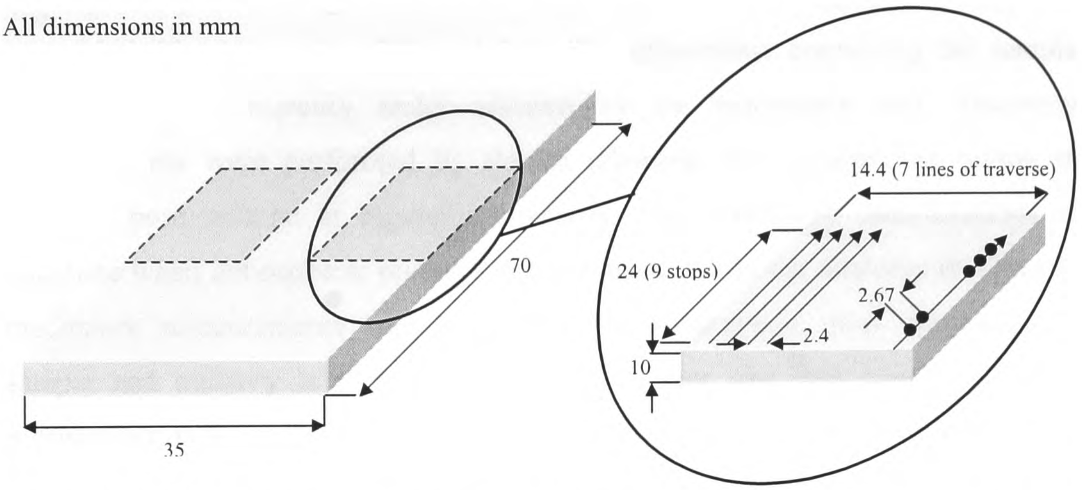


Figure 3.9 Schematic description of the test procedure followed for the ASTM C457 modified point count method.

3.4.5 Mercury intrusion porosimetry

Samples were taken from the cubes that had been water cured for 21 days and were from the same mixtures as those tested for compressive strength. To achieve consistency, a similar region of each concrete cube was sampled. This comprised the narrowest part of the typical 'hourglass' failure common in concrete cubes. Samples of mortar of 0.5-1 g were taken. The samples were dried under silica gel at 40°C until constant weight was achieved in the same manner as the concrete discs that were prepared for the sorptivity and water absorption investigation (see Section 3.4.6). Due to the large surface area to volume ratio of the small samples most of the weight loss (≈ 75%) occurred in the first 72 h of drying. After drying the samples were stored in a sealed container over silica gel to minimize any further modification of the pores by moisture ingress.

Porosity and pore size distribution measurements using the mercury intrusion technique were performed on the dry sample. Two Fisons (Italy) instruments were used for MIP, the Macropore Unit 120 and the Porosimeter 2000WS which is remotely operated via a dedicated personal computer. From each concrete mixture, four samples of mortar were tested. Each sample was weighed and then inserted into the dilatometer bulb. To ensure a good seal the neck of the dilatometer stem was smeared with silicone grease before coupling with the dilatometer bulb. The assembled dilatometer was then weighed. The dilatometer containing the sampled was filled with mercury under vacuum by the macropore unit. Macropore measurements were performed by slowly releasing the vacuum and noting the intruded pore volume at regular increments. The macropore measurements are complete when atmospheric pressure was achieved within the dilatometer. Once the macropore measurements were completed the dilatometer, now containing the sample and mercury is re-weighed. The dilatometer was then transferred to the porosimeter unit where the high-pressure measurements were performed. Before commencing the high pressure measurements the data collected so far were entered into the controlling software. The high-pressure measurements are performed automatically via the dedicated computer. The porosimeter unit has an upper pressure limit of 200 MPa and can measure pores with radii greater than 0.004 μm. From the data returned at the termination of the experiment the cumulative pore volume, threshold radius and percentage of pores with a radius < 0.05 μm were calculated. Further details of the MIP technique are mentioned in section 6.1.1 of Chapter 6.

3.4.6 Sorptivity and water absorption

The specimens used to determine sorptivity and absorption consisted of 75 mm diameter and 30 mm thick concrete discs wet cut, using a Harison M300 lathe, from the central portion of 75 diameter cylindrical cores. The cores were cut with a Qualters and Smith R3 radial drill from 100 mm concrete cubes that were cast from the same mixtures utilisized in the freeze-thaw investigations, and water-cured for 21 days. Two specimens were retrieved from each core (top and bottom sample) and the remaining outer portions were discarded (see Figure 3.10). The concrete discs were dried to constant weights in a temperature controlled drying cabinet containing silica gel. The temperature in the cabinet was kept constant at 40°C and silica gel was renewed every two days. The time required to achieve constant weight varied because of the different composition of the concrete mixtures. After drying the samples were labelled with identification codes and stored in airtight containers over silica gel to ensure moisture free storage.

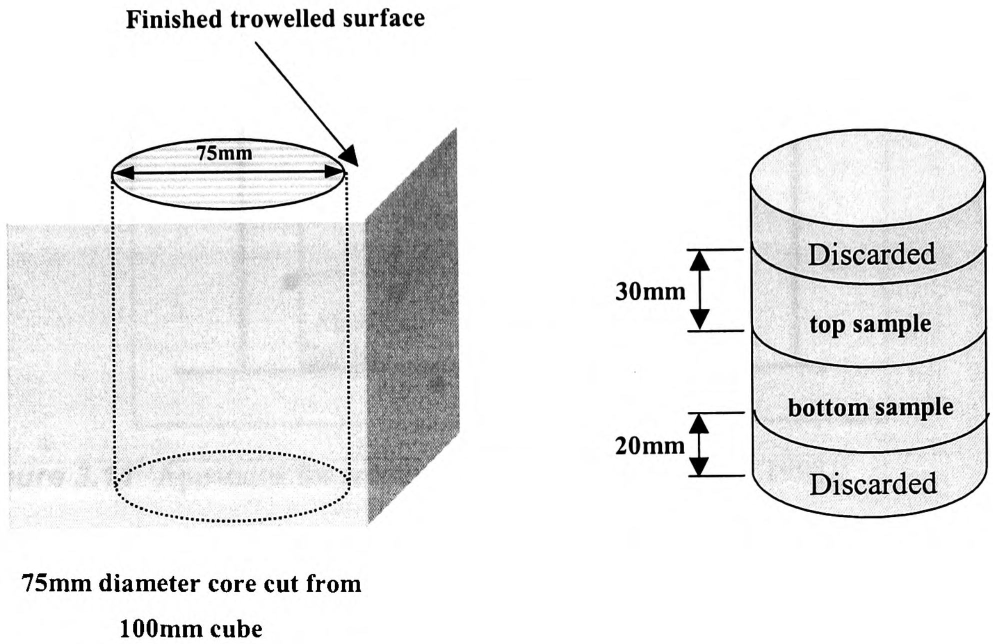


Figure 3.10 Schematic view of sample preparation for sorptivity tests.

The sorptivity of each concrete disc was determined using the specially designed and constructed apparatus shown in Figure 3.11. The system allows automatic monitoring of the water uptake experienced by the sample when its lower surface is in contact with water in a reservoir. The apparatus consists of a suspension frame constructed of rigid copper wire, which is attached to the sensor of an electronic balance. The other end of the frame is rigidly attached to a light aluminium tray containing a central hole, 75 mm in diameter. The specimen is placed centrally on the aluminium tray with the hole facilitating exposure to water at the test surface. The balance (Sartorius LC 3201D) is placed on a rigid table and is controlled by purpose written software, which is installed on a personal computer. The balance has a sensitivity of 0.001 g. The weight gain by the test specimen is automatically recorded at specified intervals. These readings are recorded by the dedicated computer system and can be retrieved, after the test is completed, in both numerical and graphical forms.

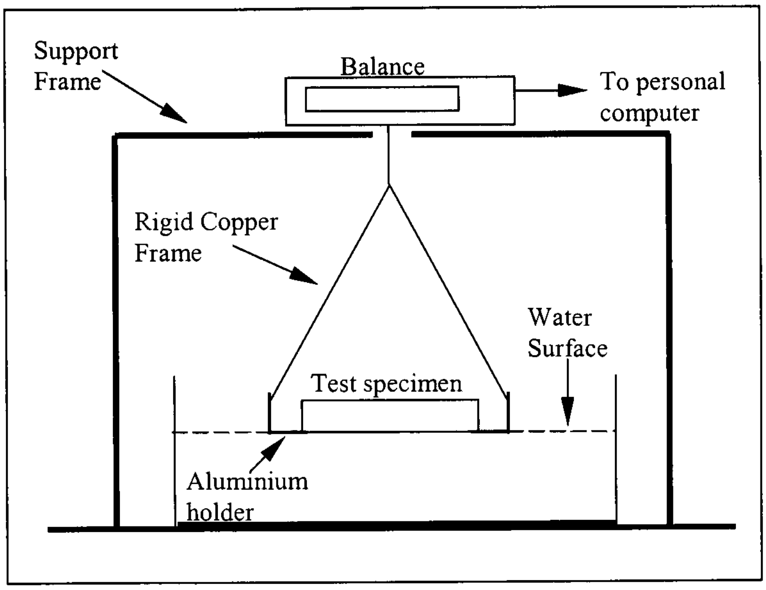


Figure 3.11 Apparatus for sorptivity tests [after Sabir et al., 1998].

After drying the specimen under test was placed centrally on the horizontal aligned aluminium tray over the water reservoir. Water, at room temperature, was then added to the reservoir until the free surface reached a level approximately 5 mm below the test surface. At this point the weight detecting system was activated, and water was added at a slow rate until the water surface was just in contact with the underside of the specimen and an increase in the balance reading was observed. This increase is due to surface tension forces and the event was used as a reference point to indicate contact of water with the test surface. The test surface was then visually examined to ensure that no air was trapped under the specimen. If this occurred, then the test was aborted and the specimen reconditioned for a repeat test. Weight measurements were taken at one-minute intervals over a total test time of approximately one hour and ten minutes, with total mass changes in the range 5-8 g. After the sorptivity experiments the disc specimens were returned to the cabinet and dried until constant weight was achieved, in order to be used for total water absorption tests. After drying, the discs were weighed and immersed in water for 24 hours, the first two hours of which the discs were partially immersed to allow water to saturate the specimen by capillary rise, thus avoiding entrapment of air. After 24 hours the concrete discs were then re-weighed in a saturated, surface dry condition and the percentage of water absorbed was calculated.

Chapter 4 – Effects of admixtures on the workability, air content and strength of concretes containing pozzolans

The Chapter is introduced with a brief review of the effect of pozzolans on workability and compressive strength of concrete, together with the influence of air-entrainment on these two parameters. The Chapter then reports the results obtained on the workability and air content in concrete containing SF, MK or FA or combinations of them and the results obtained for the compressive strength development of these concretes. Also relationships are established between superplasticizer content, air entraining agent content, workability and air content and also between compressive strength and air content.

4.1 Introduction

The utilization of FA as partial replacement material for PC, in general, gives significant improvements to the properties of concrete including reduced water demand and better workability [Dhir et al., 1988]. The spherical shape and glassy surface of most FA particles, usually finer than cement, permit greater workability or slump for equal w/b ratios. The phenomenon is attributed to an adsorption-dispersion mechanism which is similar to the action of water-reducing chemical admixtures. It has been suggested [Helmuth, 1987] that the effect of FA on the workability of concrete derives from the adherence of the ultrafine particles in the FA on to the surfaces of the positively charged areas on the cement particles. When sufficient numbers of fine FA particles are available to completely cover these areas the cement particles will be effectively dispersed and will flow more easily. Generally because of better particle packing and less water requirement, fresh concrete containing pozzolanic materials shows a reduced tendency for segregation and bleeding. Consequently, improved characteristics result with regard to cohesiveness and workability. However materials with particles of very high surface area such as SF and MK increase water demand and produce adverse effects on workability. Also workability reductions produced by MK or SF are a function of their chemical activity, which results in greater consumption of water (due to both the acceleration in cement hydration and the early pozzolanic reaction) than in the case of PC only concrete. In brief, at a given total content of cementitious material the inclusion of FA generally improves workability whereas SF and MK greatly reduce workability.

Recently research work [Zhang and Malhotra, 1995, Sabir et al., 1996] has shown that the incorporation of MK in concrete has a detrimental effect on workability with increasing replacement levels of MK producing increasing water demand. Caldarone et al. [1994] observed that although the slump of concrete containing 10% MK was reduced from that of concrete with PC only, the MK concrete required 25 to 35% less HRWRA than equivalent SF mixtures. This reduction in HRWRA demand resulted in the MK concrete having less sticky consistency and better finish than the SF concrete. Sabir et al. [1996] reported that concrete mixtures containing MK at low w/b ratios (w/b = 0.35) although they appeared relatively dry, exhibited good cohesion as reported by Caldarone et al. [1994] and compacted well on vibration. Wild et al. [1996] found it necessary to employ up to 3% SP to produce moderate slumps (75 mm) in MK concrete with w/b ratio of 0.45. In another paper Sabir [1998] conducted a series of tests on concretes containing a range of MK substitutions and emphasized the need for HRWRA. Rols et al. [1999] also reported that the utilization of MK requires higher quantities of superplasticizer compared to that in the control concrete.

FA has a relatively low surface area and pozzolanic activity, thus at normal temperatures the pozzolanic reaction is very slow, which results in slow strength development. Although reductions in strength are effected by the FA at early ages, significant enhancements may result in the long term. Some very finely divided FAs also give strength enhancement at early ages. In contrast to FA, according to Wild et al., [1996] the incorporation of MK or SF in concrete significantly enhances early strength and, up to certain replacement levels ultimate strength because of the high surface area of their reactive components (silica and alumina). Also, the ultrafine pozzolans act as fillers which contribute to the densification process and consequently to strength enhancement. The combination of MK and FA in ternary cement blends should result in a number of synergistic effects [Bai et al., 1999, 2000]. MK can compensate for low early strength of FA concrete. On the other hand FA could increase the long-term strength development of MK and compensate for the increased water demand of MK concrete.

The presence of entrained air in fresh concrete has a pronounced effect on its properties. One of these is workability, which is improved. For adequate workability, the aggregate particles must be spaced in a way that they can move past one another with relative ease during mixing and placing. In this respect, the entrained air voids are often thought of as millions of tiny ball bearings in the concrete, making the mix more workable. Typically, one might expect, for a concrete containing 5% air compared to the same non air-entrained mix, a 6% increase in the compacting factor, and an increase in slump of between 20 mm and 50 mm [Williams and Swaile, 1988]. Air entrainment additionally modifies the character of a given concrete mix, such that the consistence and mobility of the concrete is improved over that of a non air-entrained mix at the same measured workability, making it easier to place and compact. Entrained air also eliminates or minimises segregation and subsequent bleeding. In addition the presence of air voids entrapped or intentionally entrained results in a loss in strength proportional to the total volume fraction of air. A relationship has been established between the compressive strength of given concrete and its air content: for each 1% of air included there will be a decrease in strength of 5.5% [Wright, 1953].

4.2 Results and discussion

As pointed out in Chapter 3 several trial mixtures were prepared for a range of pozzolanic compositions to determine the appropriate type and dosages of superplasticiser. The results reported in this chapter relate to the concrete mixtures for which details are given in Table 3.5. These comprise mixtures with 0, 10 and

20% SF or MK and 0, 20, 30 and 40% FA. Other mixtures incorporated combinations of FA and MK to produce ternary blends with several combinations of PC, FA and MK. All the ternary blends had ratios of FA:MK of either 3:1 or 1:1.

The mixtures were designated according to the pozzolan replacement level and type and the dosages (2 digits) of the superplasticiser and air entraining admixture. The pozzolans designation was abbreviated to a single letter i.e. S for SF, M for MK and F for FA. For example 5S 35/09 (Table A.1 in Appendix A) indicates a mixture with 5% SF replacement of Portland cement with 0.35% superplastisizer and 0.09% air entraining agent. In the case of the control concrete, the designation was prefixed by the letters CON, e.g. CON 31/06 (Table A.2 in Appendix A) designates a control concrete with 0.31% superplasticizer and 0.06% air entraining agent. This system of designation is followed throughout the thesis.

4.2.1 Dosage requirements for air entraining agent

The effects of SF and MK on the dosage requirements of air entraining admixture to obtain an air content of about 7.5%, for a given dosage of superplasticiser were examined first. This study involved concrete mixtures with partial PC replacements of 0, 5, 10, 15 and 20% SF or MK containing a constant dosage of 0.35% superplasticiser. The workability, as measured by the slump, and the air content of the fresh concrete are given in Table A1 of Appendix A. Table A1 clearly shows that a constant air content can be achieved, albeit at the expense of a considerable variation in slump (45-210 mm).

A comparison of the effects of SF and MK on the dosage of air entraining agent needed to attain 7.5 ± 0.6% air content of the fresh mix is shown in Figure 4.1. The results represented in this figure are given in Table A1. A constant amount of superplastisizer of 0.35% by mass of the binder was adopted for both the SF and MK mixtures. The dosage of air entraining admixture required to produce a given volume of air in concrete containing more than 5% SF or MK, as partial mass replacement for PC, increases markedly with increasing amounts of SF or MK. The admixture requirement rises very sharply from 15 to 20% of SF or MK, indicating even higher air entraining admixture demand for higher amounts of the two pozzolanic materials.

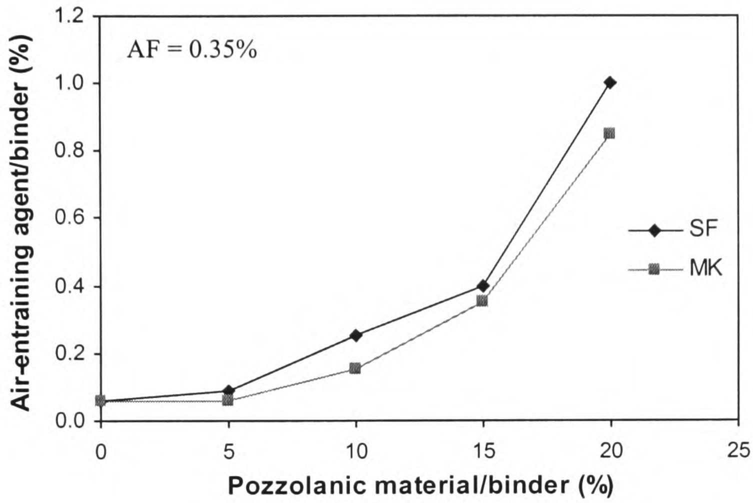


Figure 4.1 Comparison of the effect of SF and MK on the dosage of air entraining agent to obtain 7 ± 0.6 % air content in the fresh concrete.

The trend of increase is identical for both SF and MK concretes. However the SF concrete is more demanding in air entraining agent than MK concrete. This is primarily due to the higher specific surface of SF which leads to more air entraining agent being adsorbed and fewer molecules of the agent available to be adsorbed at the air-water interfaces. The carbon content of SF (Table 3.1) will also contribute to this additional adsorption. The measured slumps (Table A.1) for these mixtures were in the ranges 45-210 mm and 50-210 mm for the SF and MK concretes respectively. Figure 4.2 shows the variations in the slump with the level of pozzolanic replacements. The results demonstrate the higher water demand of SF as compared to MK, as the replacement level increases. The inconsistency in the results obtained for the 20% replacements is attributed to specimen variability.

4.2.2 Dosage requirements for superplasticizer

Another set of concrete mixtures with 0, 5, 10, 15 and 20% SF or MK were prepared to examine the dosage requirements of superplasticiser to obtain about 6.0% air content for a given dosage of air entraining agent, i.e. 0.06% for all the pozzolanic additions employed. The data for slump and air content obtained from this series of tests are given in Table A.2 (Appendex A), which shows similar slumps (about 100 mm) for all mixtures. This part of the investigation involved preparation of a large number of concrete mixtures and Table A.2 gives only those mixtures with a fixed AE3 content that gave the same slump and air content values.

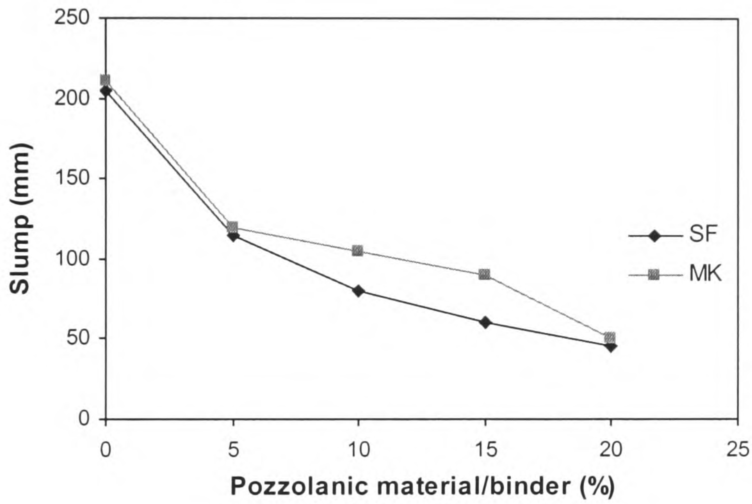


Figure 4.2 Comparison of the effect of SF and MK on the slumps obtained for concretes shown in Figure 4.1.

The relationships obtained between the superplasticizer dosage requirement and the levels of SF or MK are given in Figure 4.3. In agreement with the air entrainment dosage requirements (Figure 4.1), SF is also more demanding in superplasticizer compared to MK. The results presented in Figure 4.3 were achieved under a constant dosage of air entraining agent (0.06%) and the target air content was achieved even at the higher cement replacement levels. This suggests that the presence of superplasticizer enhances the ability of the air entraining agent to entrain air in concrete containing these two pozzolanic materials possibly by competing with the latter for surface adsorption sites.

4.2.3 Workability and air content of fresh concrete

This section gives the results of a detailed investigation of the effects of SF, MK and FA on the workability, air content and compressive strength of concrete for several dosages of the two admixtures, i.e. superplasticiser and air entraining agent. The numerical data obtained from this investigation are given in Tables A.3-A.9, in Appendix A. The sections below give a discussion of the results on the basis of pozzolans used.

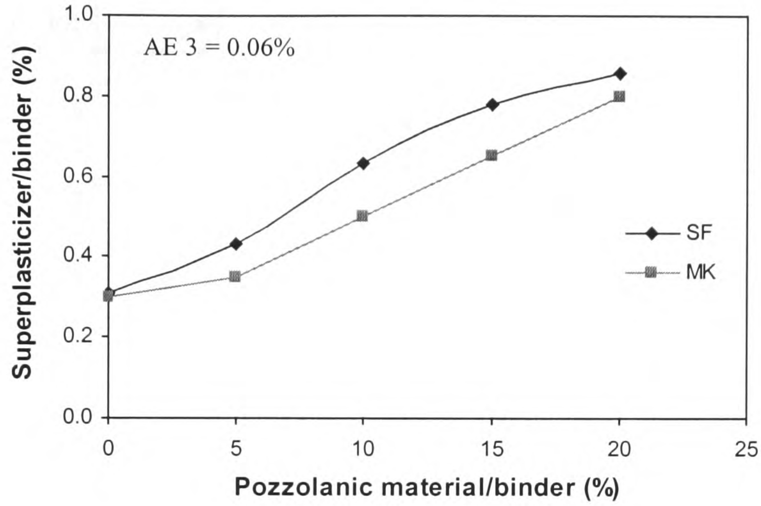


Figure 4.3 Comparison of the effect of SF and MK on the dosage of superplasticizer required to obtain 6 ± 1 % air content and 100 ± 20 mm slump in the fresh concrete.

Silica fume concrete

The test results characterising the effects of the air entraining agent on the slump, compacting factor and air content of SF concrete are presented in Figure 4.4. The data presented are given in Table A.3, which also gives the dosages of superplasticiser used. These were 0.3 and 0.5% for the control and SF concretes respectively. In all cases, the addition of air entraining agent resulted in an improvement in the workability as manifested by the increase in the slump and compacting factor (see Figures 4.4(a) and (b)). For up to 0.12% air entraining agent the control and 10% SF concretes had similar slumps, the increase in water demand of the SF being compensated by the additional superplasticiser employed in the SF concrete. Although higher dosages of air entraining agent produce significant increases in the slump of the control concrete, this influence is not manifested in the SF concretes the slumps of which remain more or less constant. This behaviour could

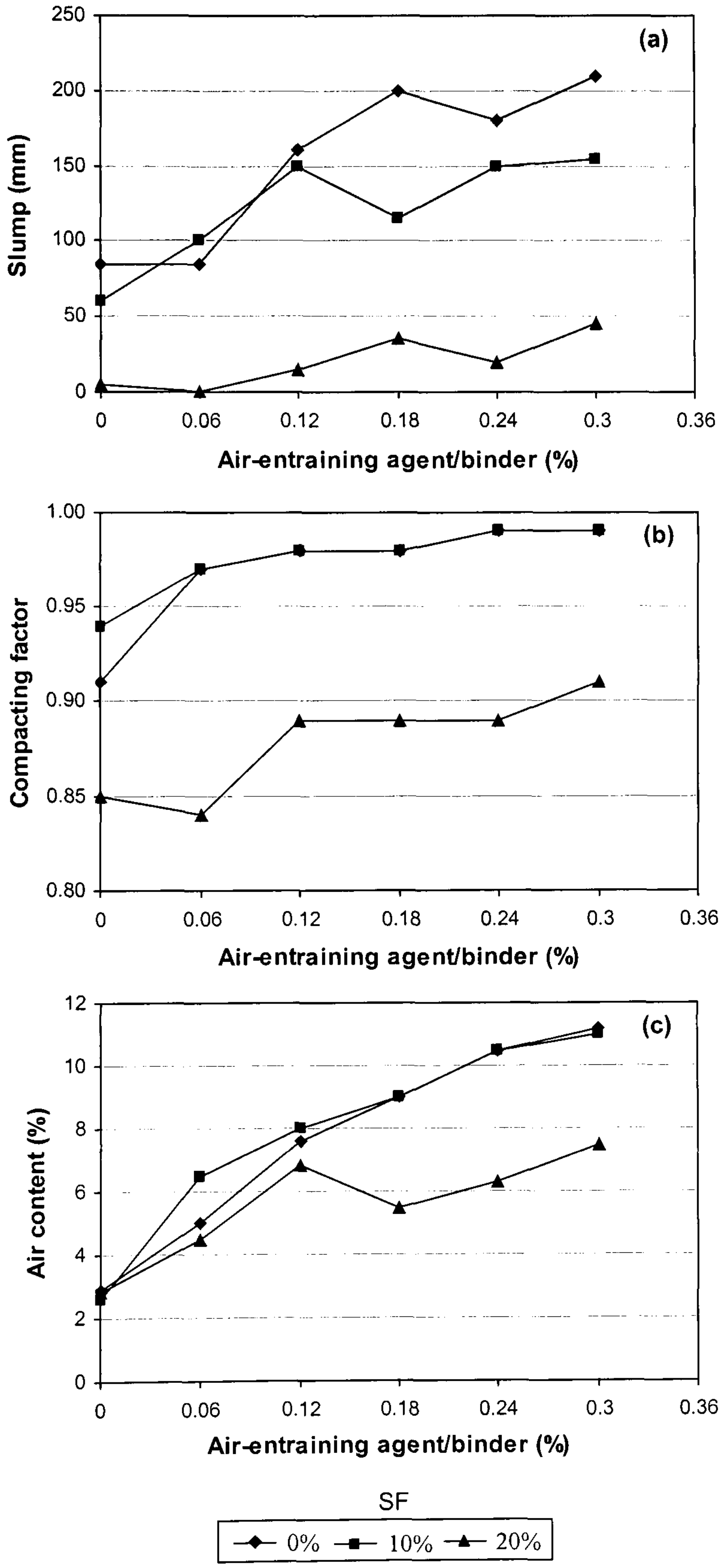


Figure 4.4 Effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of control and SF concrete with 0.3 and 0.5 % superplasticizer respectively.

be explained by the greater diffusion effected by the increased concentration of air entraining agent with more of the admixture being adsorbed by the very fine SF particles, thus eliminating the role that the additional air entraining agent played in increasing the workability. In the case of the 20% SF concrete, the improvement in workability, as measured by the slump, attributed to the air entraining agent continues for a higher dosage, i.e. 0.18%. As was expected, the 20% SF concrete exhibited slumps which were much lower than those of the 10% SF. This is due to the steep increase in the water demand caused by the additional 10% PC replacement by SF. Similar behaviour can be observed for the compacting factor results, with the exception that the test did not detect differences between the control and the 10% SF concrete when air entraining agent was used.

Figure 4.4(c) gives the variations in the measured air contents with increasing dosage of air entrainment agent. The results clearly demonstrate the efficiency of the admixture in entraining air in all the concretes investigated. It is seen that sharp rises in the air contents are obtained for dosages up to 0.12%. Dosages greater than 0.12% have less influence on air content in the case of 20% SF whereas the air content of the control and 10% SF concretes show continuous increase. A similar behaviour was encountered by Carette and Malhotra [1983a] who found it difficult to entrain more than 6% air in concretes with 20% SF. The marked increase in workability of the control and 10% SF concretes with increasing air entraining admixture up to 0.12% (Figure 4.4(a)) is related to the increase in the volume of entrained air over this range (Figure 4.4(c)) which generates greater mobility.

It is interesting to note that all the concretes without air entraining agent had the same volume of naturally entrapped air. Generally, because of the filler effects of the very small SF particles, its use in concrete results in a more densified matrix with reduced entrapped air. It is thought that in the present study the expected reduction in the air content caused by the SF is compensated for by the additional superplasticiser used as compared to that in the control. Superplasticisers are known, sometimes, to cause more air to be entrapped in the system. The increased entrapped air due to the superplasticiser is also manifest in the 10% SF concretes in which air entraining agent is added. This effect, however, reduces when the SF level is increased to 20%, where the absorption effects, described above, due to the fine SF particles play a more significant role in reducing the measured air content of the fresh concrete. It is to be emphasised that both the 10 and 20% SF concretes contained the same amount of superplasticiser as a fraction of the total binder, i.e. 0.5%. The sharp reductions in the air contents of the SF concretes with 0.18% air entraining agent (or increases at 0.06%), also observed in the slump measurements (Figure 4.4(a)), may be indications of instability or are attributed to sample variability. The results shown in Figure 4.4(c) give good indications as to the dosages of the air entraining agent required to obtain the desired air contents in the fresh concrete. For example in order to entrain 6% air, dosages of air entraining agent of 0.06 and 0.12% are required for 10% SF and 20% SF concretes, respectively.

Metakaolin concrete

Figure 4.5 shows the variations in slump, compacting factor and air content with increasing air entraining agent for the control and MK concretes. The actual data are given in Table A.4. The same replacement levels, i.e. 10 and 20% MK, were employed as those used in the SF concretes discussed in the previous section. Also the dosage of superplasticiser used for the MK concrete was the same as that used for the SF concrete, i.e. 0.5% of the mass of the total binder. As in the case of the SF concretes, the air entraining agent resulted in increased workability of all the MK concretes investigated. Indeed the rate of increase in slump and compacting factor of MK concretes with air entraining agent content are seen to be somewhat greater than those obtained for SF concrete. It is also noticeable that the improvement in workability occurs for an increased range of dosages of air entraining agent as compared to that obtained for SF concrete. In fact the concrete with 10% MK exhibited a collapsed state when the air entraining agent was increased beyond 0.18%. This may be due to the somewhat coarser particle size of MK as compared to those of SF resulting in less admixture being adsorbed by the pozzolan and increased dispersal. As with SF, MK also has increased water demand over that of PC only concrete, but to a reduced level. This is confirmed by the significant increases in slump measurements of MK concrete over those obtained for SF concrete (Figure

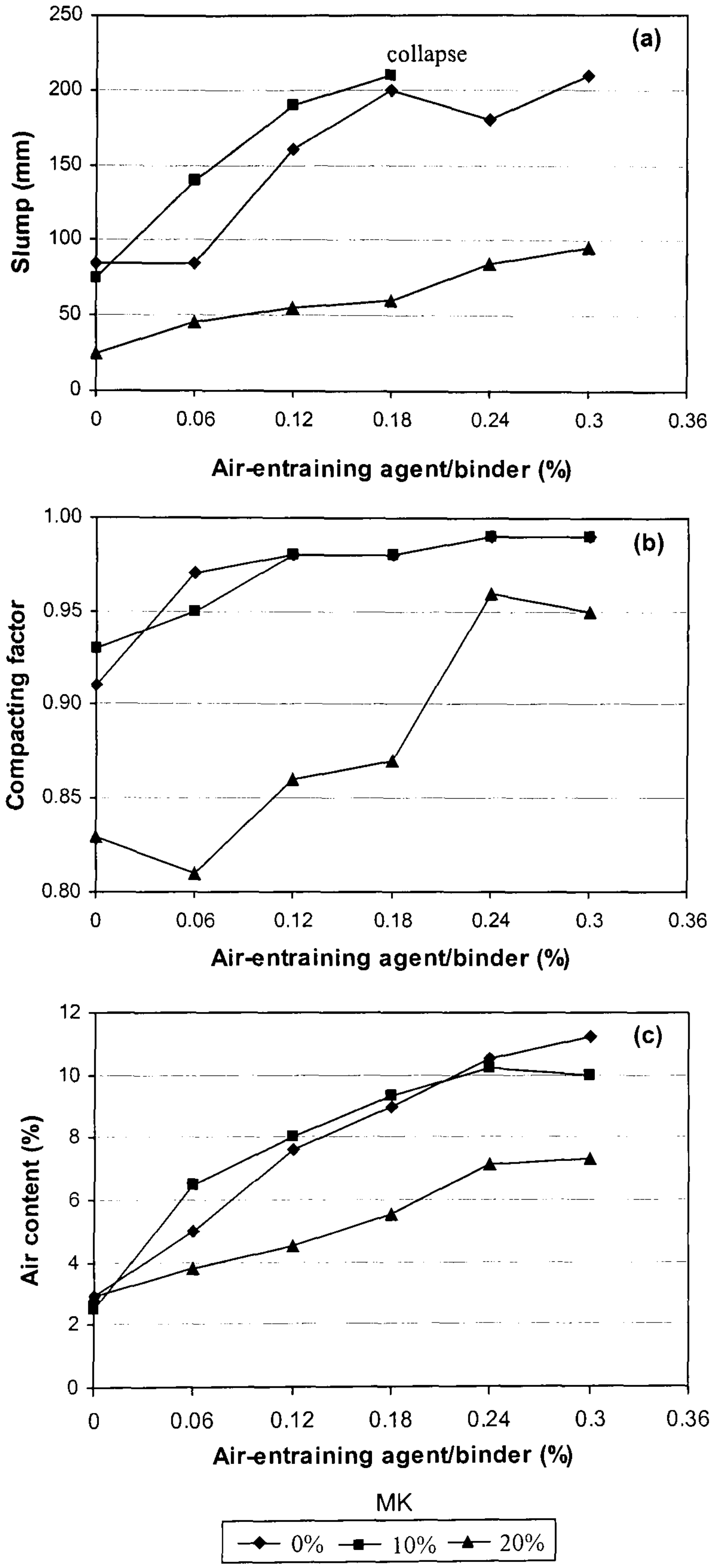


Figure 4.5 Effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of control and MK concrete with 0.3 and 0.5 % superplasticizer respectively.

4.4(a)) for PC replacement levels of 10 and 20%, all containing the same level of superplasticiser, i.e. 0.5%. Behaviour with respect to compacting factor results for MK concretes, is similar to those exhibited by SF concretes (Figure 4.4(b)) i.e. this test did not detect differences between the control and the 10% MK concretes when air entraining agent dosages greater than 0.06% were employed.

Figure 4.5(c) gives the variations in the measured air contents with increasing air entrainment agent. Again as with SF concrete, the results show the efficiency of the admixture in entraining air in such concretes. It is seen that steady increases in the air contents are obtained for dosages up to 0.24%. This optimum limit is significantly greater than the limit of 0.12% dosage exhibited by SF concrete. Again as with the SF concretes, MK concretes and the control concrete without air entraining agent exhibit the same volume of naturally entrapped air. This is due to the role of the increased level of superplasticiser, from 0.3 to 0.5%, in entrapping air in the system. The increased entrapped air due to the superplasticiser is also manifest in the concretes dosed with air entraining agent as portrayed by the 10% MK concrete which exhibits almost identical air contents to those of the control. The role of the superplasticiser, at a dosage of 0.5% of binder mass, played in entrapping additional air to the accidental air normally entrapped diminishes in extent as the MK level increases to 20%. At such high levels of MK the increased adsorption of the admixture by the greater specific surface of the binder becomes dominant resulting in reduced air contents. It is observed that MK concrete gives more consistent changes in air content, with increasing air entraining agent, than those obtained for SF concrete. All the measurements presented in this study were made by the candidate himself using the same equipment and under the same operating conditions. For these reasons it is found difficult to attribute the lack of consistency in the results obtained for the SF concrete (Figure 4.4(c)) as being due to variability of controls. Rather it is thought that the behaviour is an indication of some instability that is inherent to the system examined. It is planned that a repeat of some of the tests will be conducted during the study. If the results of these tests reproduce the observations already made, then it would appear that the admixtures used are more compatible with MK than they are with SF. According to Figure 4.5(c), 6% air content in the fresh concrete requires dosages of approximately 0.06 and 0.20% air entraining agent in the 10 and 20% MK concretes, respectively. The results also indicate that it would be difficult to entrain air in excess of about 6%, (though normally not desirable) in 20% MK concrete even with high dosages of air entrainment agent. In the case of 10% MK, air contents in excess of 10% may be entrained. Similar results were encountered in the case of the SF concretes. This behaviour is attributed to the dispersal effects when high dosages of air entraining agent are used in conjunction with high pozzolan levels, leading to greater adsorption rates.

Fly Ash concrete

Figure 4.6 gives the variations in slump, compacting factor and air contents for the FA concretes. In these concretes the PC was replaced by 20, 30 and 40% FA all of which contained the same dosage of superplasticiser (i.e. 0.3%) including the control concrete, as shown in Table A.5. Because FA generally imparts additional workability when used as a partial PC replacement in concrete it was decided to employ only a small dosage of superplasticiser, i.e. that used in the control concrete. It was also considered that this low level of superplasticiser would maintain adequate workability in the planned series of mixtures containing both MK and FA. For the control and 20% FA concretes the slump (Figure 4.6(a)) increases as the level of air entraining agent increases up to 0.18%. Generally, for a given dosage of air entraining agent (up to 0.18%), the slump increases as the FA level increases. Larger dosages of air entraining agent seem to have little or no effect on the slump for all FA levels. Broadly similar but less differentiated behaviour is observed for the compacting factor results in Figure 4.6(b). In contrast, Figure 4.6(c) shows large reductions in air content caused by the incorporation of FA, irrespective of the dosage of the air entrainment agent. This reduction increases as the FA level increases for all dosages of the admixture. Although moderate increases in air content are obtained for the 20% FA concrete, albeit at the cost of high dosages of the admixture, little or no gain in air content is exhibited by the 30 and 40% FA concretes. This may be due to the absorption effects caused by the unburnt carbonv that may be present in FA. These results indicate that at low levels (up to 0.18%)

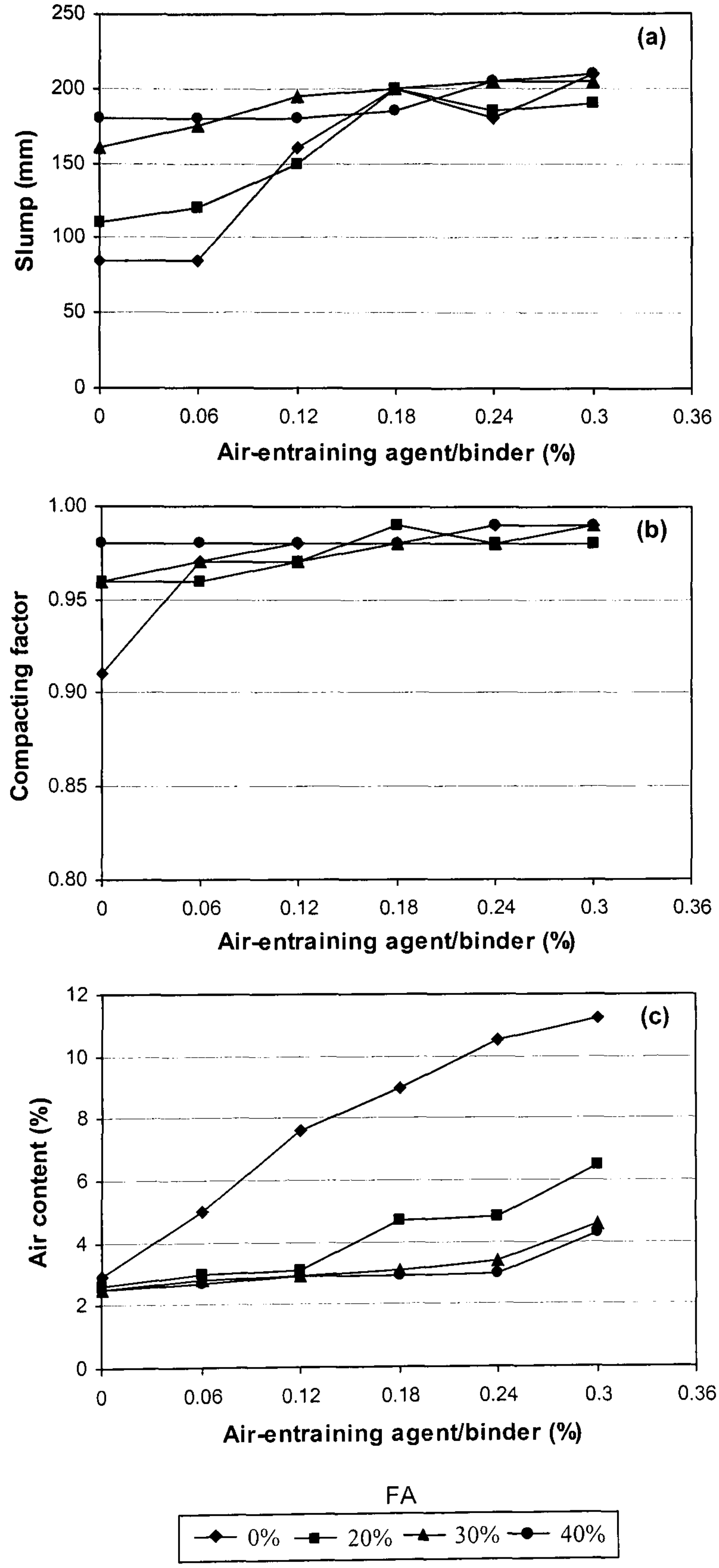


Figure 4.6 Effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of control and FA concrete with 0.3 and 0.5 % superplasticizer respectively.

the admixture acts more effectively as a lubricating rather than an air entraining agent.

Concrete with PC replacements by 20% SF, MK or FA

In this section a direct comparison of the results for the slump, compacting factor and air contents for the control and the 20% SF, MK and FA concretes is made. The results are shown in Figure 4.7, again expressed as a function of the dosage of the AEA. It should be noted that the control and FA concretes contained 0.3% SP compared to a dosage of 0.5% in the SF and MK concretes. It can be seen that for this level of PC replacement, the workability improvement due to air entrainment is evident for all concretes. The control and FA concrete had identical slumps and compacting factors except at low air entrainment dosages (0-0.06%) where the FA concretes exhibited higher slumps. The incorporation of SF and MK results in marked reductions in slump over those of the control and FA concretes. It is also clear that with respect to slump loss SF has a much higher water demand than MK. Both SF and MK concretes show steady increase in slump as the dosage of air entraining agent is increased from 0.06 to 0.3%. Similar behaviour is shown by the control and the FA concretes as determined by the compacting factor test, except that the increase in workability is found to be very modest as compared to that obtained by the slump test. Although the compacting factor test shows steeper increases in workability in the SF and MK concretes than those obtained by the slump test, the results indicate that for 0-0.18% air entraining agent the SF concrete is easier to compact than MK concrete. This may be attributed to the cohesion forces imparted by the MK to the concrete.

The results shown in Figure 4.7(c) for the air contents show that all pozzolans have a negative effect on the volume of air-entrained in the fresh concrete. The greatest reductions in the air contents are exhibited by the FA concretes for all dosages of air entraining agent, 0-0.3%. SF and MK appear to cause similar reductions in air contents for all dosages of air entraining agent with the exception of the SF concrete with 0.12% dosage which shows a sharp rise in the measured air content.

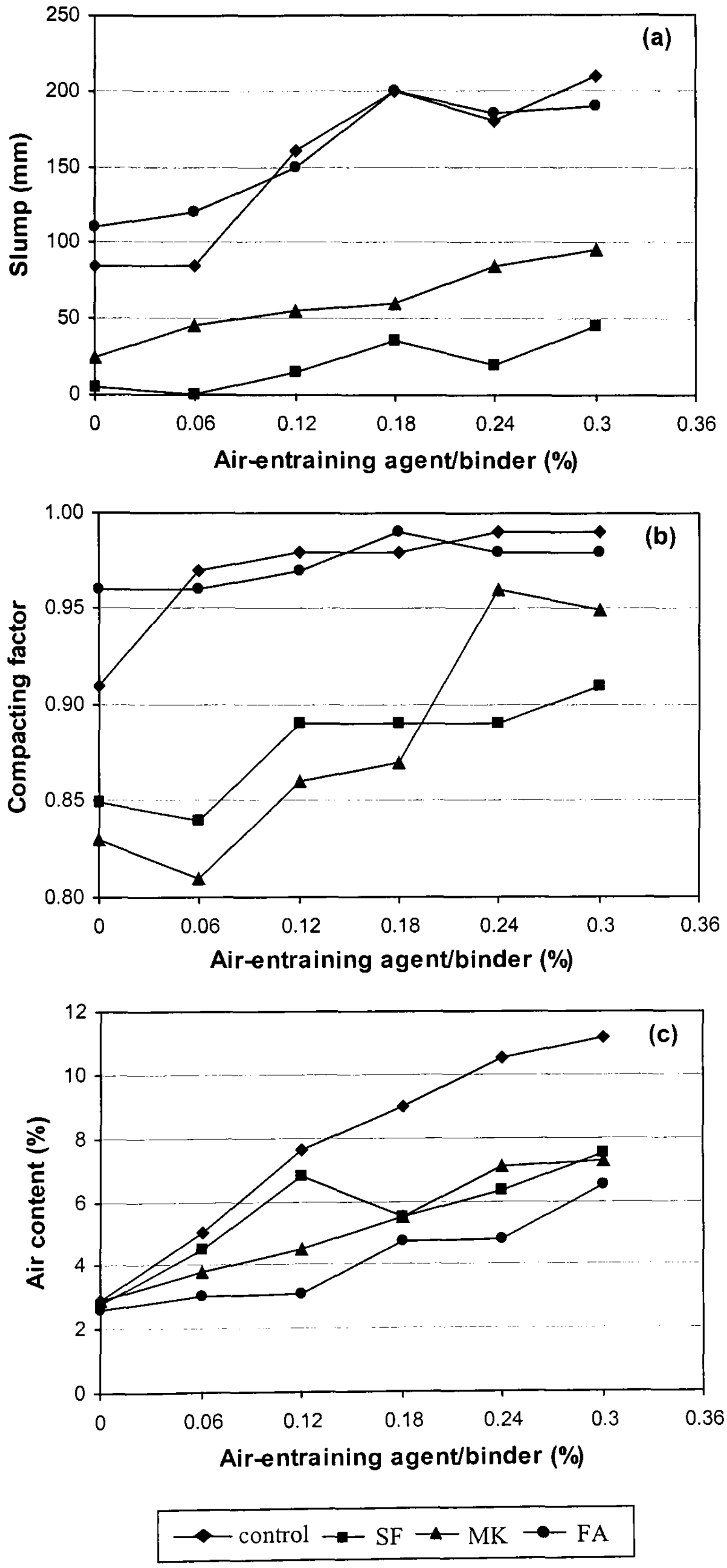


Figure 4.7 Comparison of the effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of control and 20% SF, MK and FA concrete.

<u>Concrete with PC replacement by blends of FA and MK</u>

The test data for the fresh concrete in which the PC was replaced by blends of FA and MK are given in Tables A.6-A.8. Figures 4.8-4.10 give the changes in slump, compacting factor and air content with air entraining agent for concretes with a total PC replacement of 20, 30 and 40% respectively. The FA was used as the main PC replacement pozzolanic material which was then blended with MK in the ratios 1:3 and 1:1. Figures 4.8(a) and (b) show that for a total replacement of 20% the slump and compacting factor exhibit marked increases as the air entraining agent dosage increases up to 0.3% irrespective of the blend composition and this corresponds with marked increases in the amount of air-entrained (Figure 4.8(c)). Figures 4.8(a) and (b) also show, as would be expected, a systematic decrease in workability as the MK content increases. Similar effects in workability are produced in the concrete with total replacements of 30 and 40% (Figures 4.9 and 4.10) except that only marginal increases, if any, are exhibited as the air entraining agent dosage increases and this corresponds with only marginal increases in the amount of air-entrained. Thus the beneficial effects on workability due to the air entraining agent are lost as the total replacement increases. It is also of interest to note that the reduction in slump (Figures 4.8(a), 4.9(a) and 4.10(a)) when the PC is blended with MK and FA in the ratio 1:3, increases with increase in total replacement relative to the PC-FA concrete. Although broadly the compacting factor behaved in a similar manner to the slump, the results for the 30% and 40% total replacements were not consistent with those obtained at 20% total replacement, where the values converged to one point. This unexpected behaviour may be an indication of the unsuitability of the test for the concretes examined.

Figure 4.8(c) shows that the air content of the fresh concrete increases steadily up to about 0.12-0.18% air entraining agent and then increases sharply for further additions, irrespective of the blend composition. Figure 4.9(c) for a total PC replacement of 30% shows that the transition from a steady increase to sharp increase takes place at a dosage of air entraining agent of 0.24%. For a 40% total replacement (Figure 4.10(c)) although more significant differences exist between the concretes

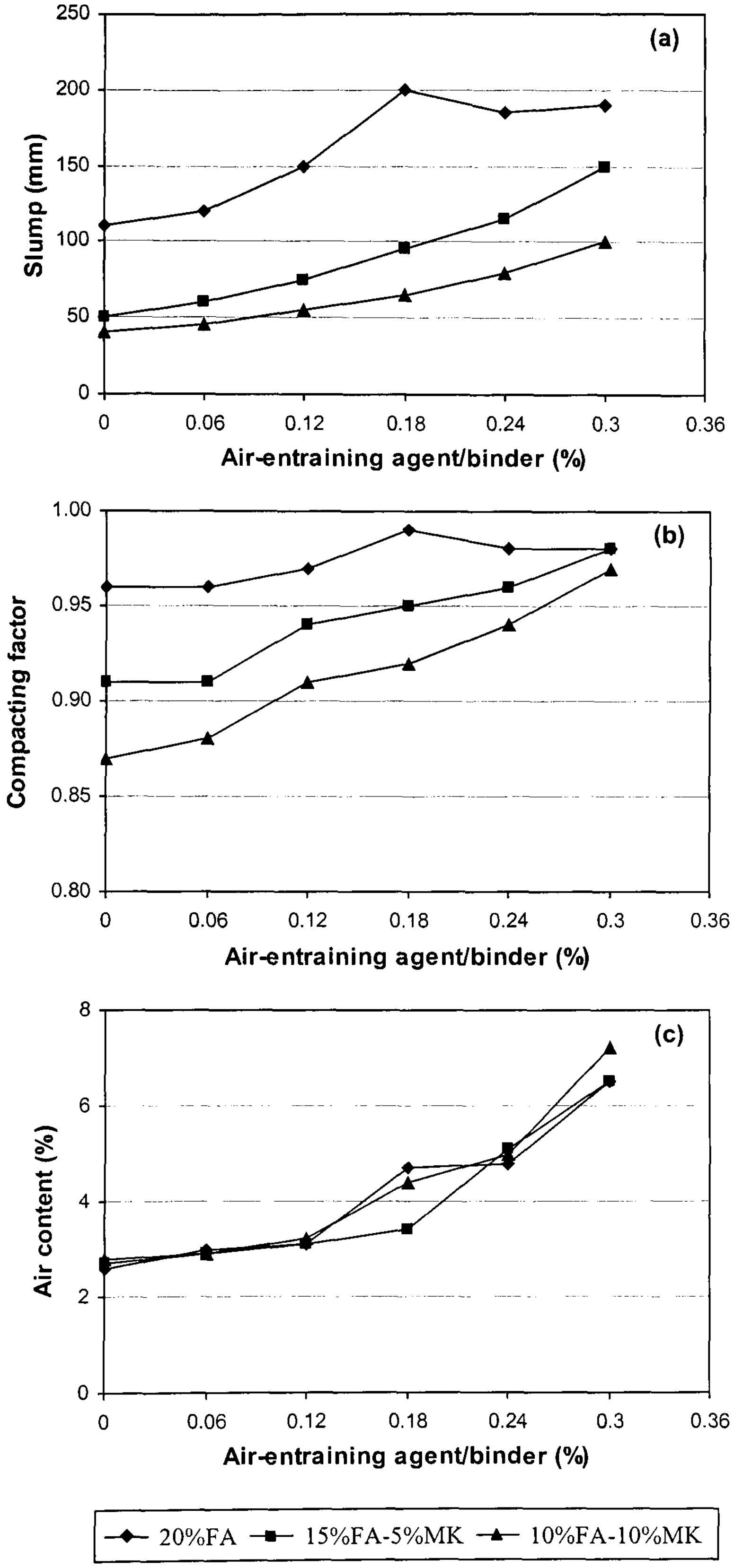


Figure 4.8 Comparison of the effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of FA-MK concrete: 20% total replacement.

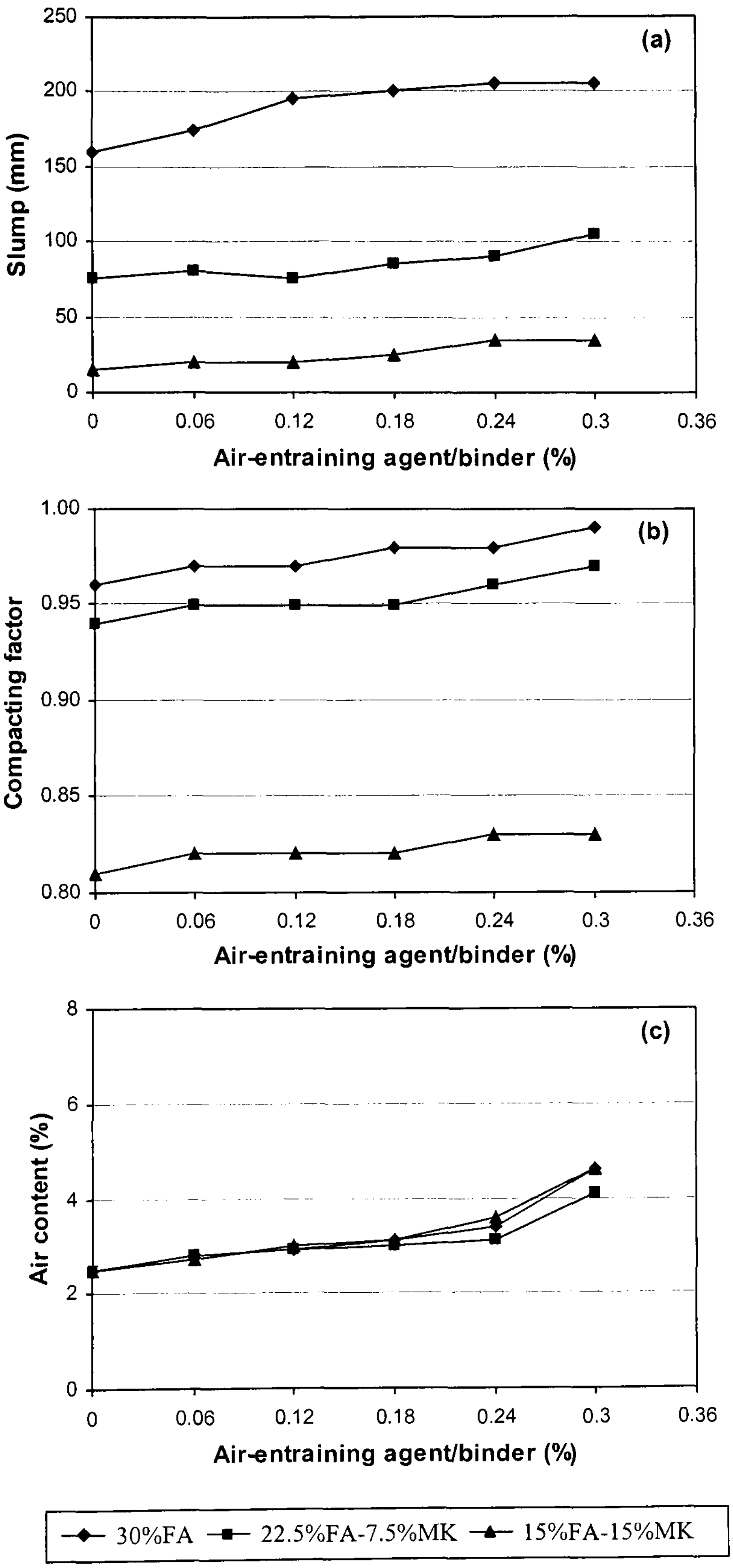


Figure 4.9 Comparison of the effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of FA-MK concrete: 30% total replacement.

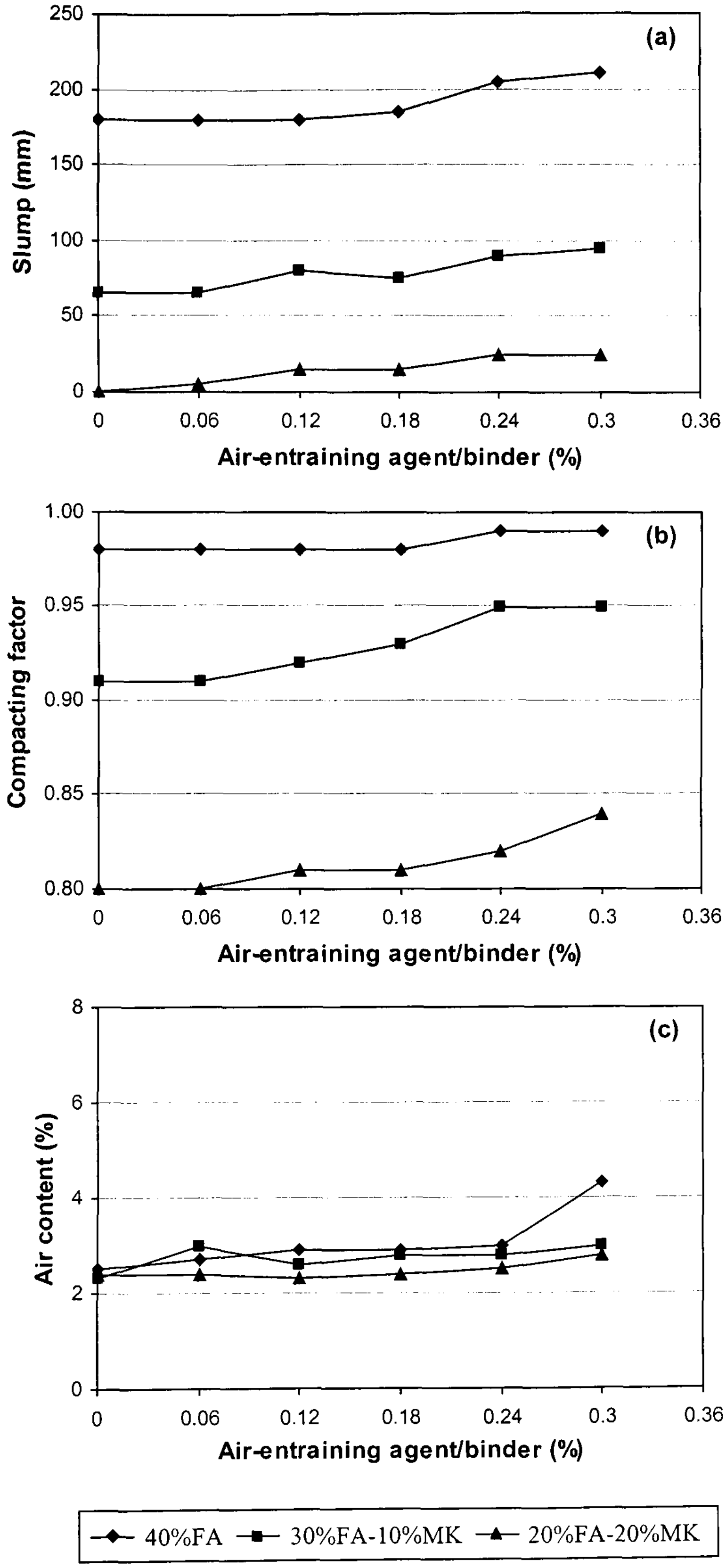


Figure 4.10 Comparison of the effect of air entraining agent on (a) slump (b) compacting factor and (c) air content of FA-MK concrete: 40% total replacement.

with differing blend proportions, there appears to be little change in the air contents as the air entraining agent dosage increases.

4.2.4 Effect of MK/FA ratio

Figures 4.11, 4.12 and 4.13 give plots of slump, compacting factor and air content versus MK/PFA ratio respectively, for the three total replacement levels of 20, 30 and 40%. Figure 4.11 shows consistent reductions in the slump as the MK/FA ratio increases. This is true for all total replacement levels and at all dosages of air entraining agent. It may also be observed that the slumps show a less linear behaviour with MK/FA ratio and fall more sharply as the total replacement level increases. For a given MK/FA ratio, the slumps show wider and systematic variations effected by the different dosages of the air entraining agent at a total replacement level of 20% than those exhibited at the 30 and 40% replacements. Similar results were obtained by the compacting factor test as shown in Figure 4.12.

The comparisons for the air contents are shown in Figure 4.13. Irrespective of the total PC replacement level and with few exceptions, the MK/FA ratio has virtually no influence on the measured air content. Also for a given MK/FA ratio, there are smaller variations in the air contents attributed to the dosage of air entraining agent, as the total replacement increases. At 20% total replacement the air contents vary between 2.6 and 7.2% (Tables A5 and A6) whereas at 30 and 40% replacements these are restricted to between 2.3 and 4.6% (Tables A5, A7 and A8). This suggests that at high replacement levels, irrespective of the MK/FA ratio, the entrainment of air is difficult.

4.2.5 Compressive strength

Effects of air content

In Figure 4.14 the 28-day compressive strengths for the control and SF, MK and FA concretes are shown as a function of the air content. The results show considerable linear and systematic reductions in the strength of SF and MK concretes due to increase in the entrained air content. This is attributed to the fact that with increased

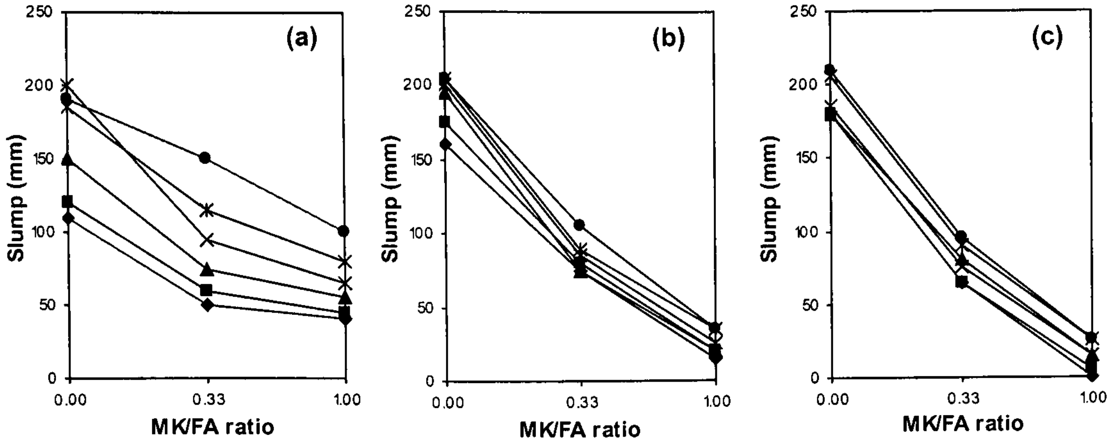


Figure 4.11 Comparison of the effect of MK/FA ratio on slump of FA-MK concrete at (a) 20% (b) 30% and (c) 40% total cement replacement.

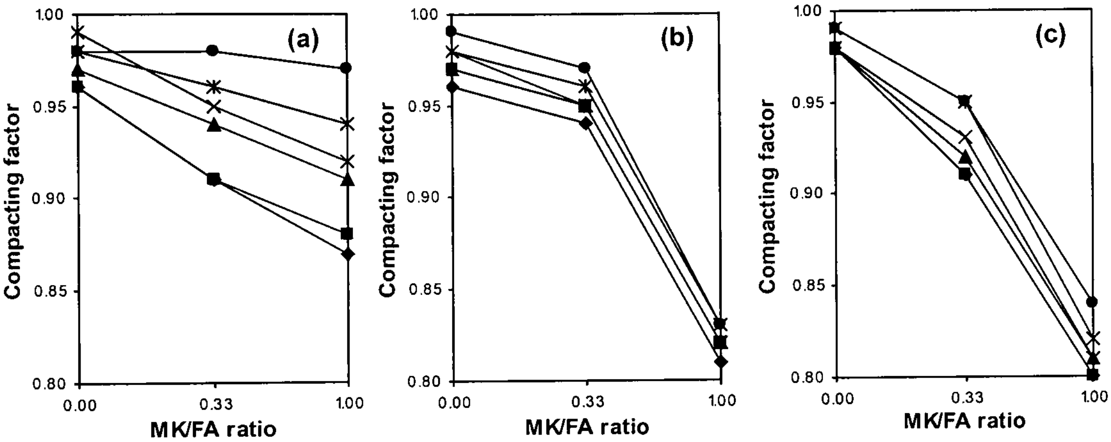


Figure 4.12 Comparison of the effect of MK/FA ratio on compacting factor of FA-MK concrete at (a) 20% (b) 30% and (c) 40% total cement replacement.

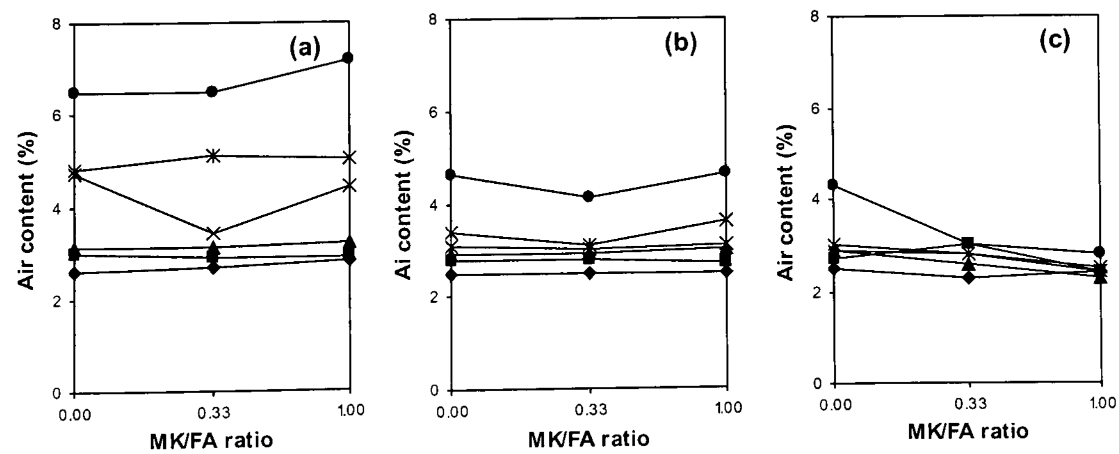


Figure 4.13 Comparison of the effect of MK/FA ratio on air content of FA-MK concrete at (a) 20% (b) 30% and (c) 40% total cement replacement.

AEA dosage

0% 0.06% 0.12% 0.18% 0.24% 0.30%

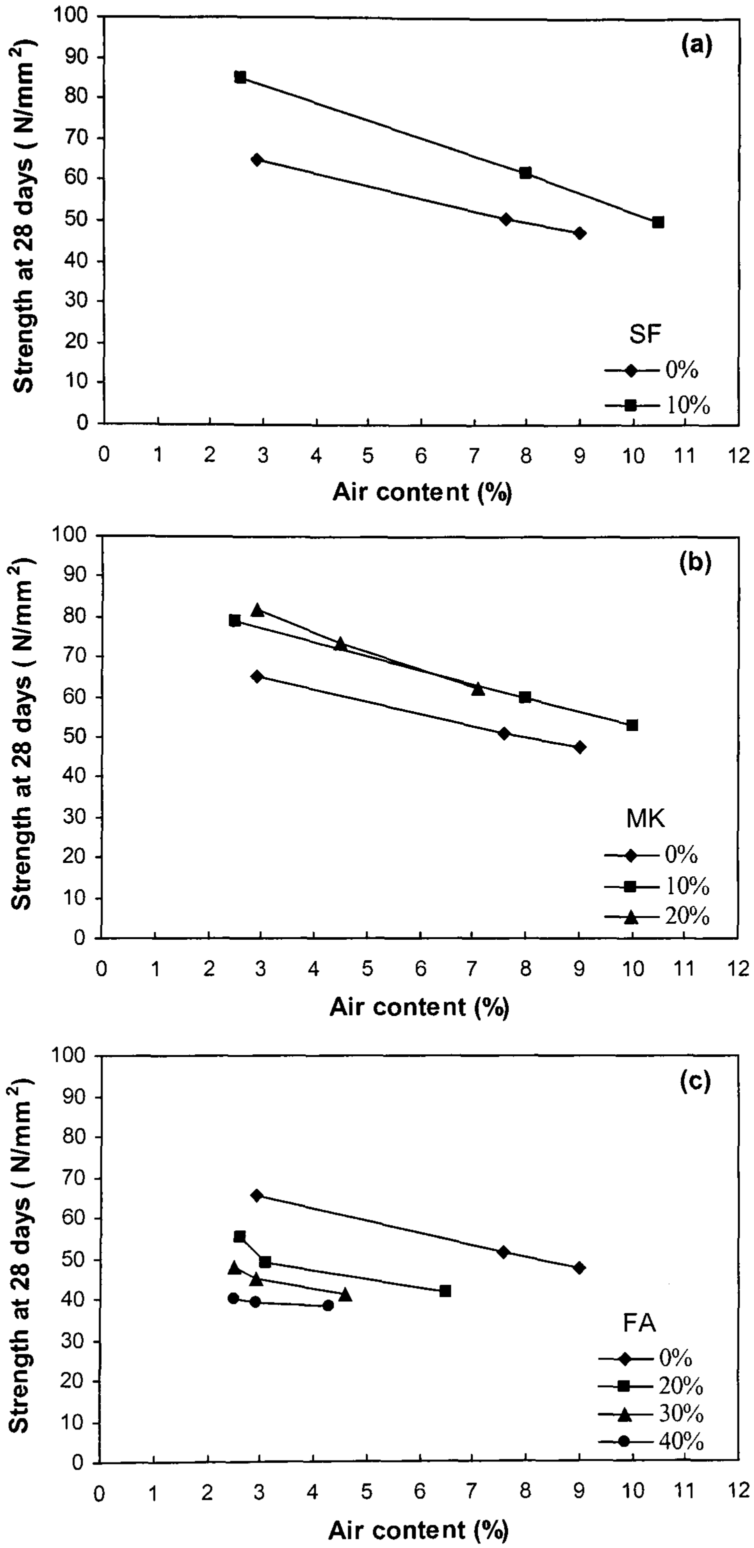


Figure 4.14 Effect of entrained air content on the 28-day compressive strength of (a) SF (b) MK (c) FA concrete.

entrained air the structure becomes more porous resulting in strength reductions. Similar relationships for FA-MK concretes are observed in Figure 4.15, which also indicates the relative positions of the trend lines for concretes of various compositions. Figure 4.15(a) shows that a 10% FA-10% MK concrete gives strengths that are greater than the control concrete. Furthermore, Figure 4.15(b) shows that concrete of similar strengths can be obtained by a larger total replacement (30%) with a blend of 15% FA and 15% MK. Even a higher PC replacement (40%) may be employed (Figure 4.15(c)) to obtain strengths similar to those of the control.

Figure 4.16 is developed to give the percentage reductions in the strength at all curing ages, for concretes incorporating SF, MK or FA attributed to air content increases. For example when the air content in 10% SF concrete increases from 2.6 to 10.5% (Table A.3), i.e. increases by 304% (Table A.9), there is a reduction in the 28-day compressive strength of 41%. The reduction in the 28-day strength of the 10% MK concrete corresponding to an increase in the air content from 2.5 to 10.0% (Table A.4) or 300% increase is 33% (Table A.9). Similar effects are produced in the FA concretes. For example an increase in air content from 2.6 to 6.5% i.e. an increase of 150%, in 20% FA concrete gives a reduction in the 28 day strength of 24% (Table A.9). The results show that irrespective of the curing time, the percentage reductions in strength due to the increase in air content are more or less the same for all concretes considered in the present study. It is also seen that the relationship between the percentage reductions in strength and the percentage increases in strength is almost linear with the exception of those reductions corresponding to small increases in the air content of the fresh concrete. From the gradient of the curve it is estimated that for every 12% increase in air content there is a 1% reduction in strength.

Effects of pozzolans

Figure 4.17 gives a direct comparison of the strength development between the control and 20% SF, MK and FA concretes. The concretes chosen for this comparison were those with more or less the same air contents. These ranged between 6.8 and 7.6%. The curves clearly demonstrate that at this replacement level

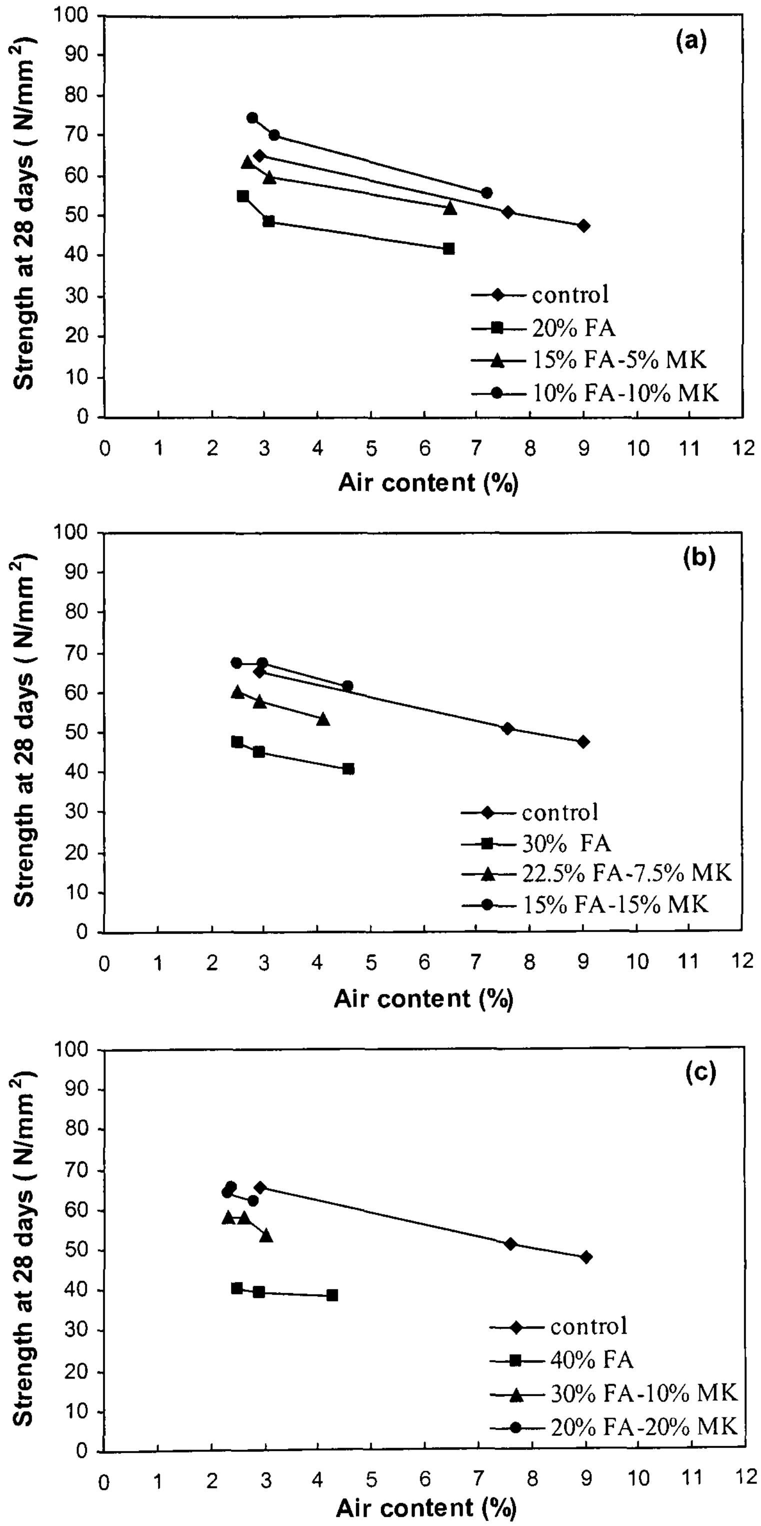


Figure 4.15 Effect of entrained air content on the 28-day compressive strength of (a) 20% (b) 30% (c) 40% total cement replacement FA-MK concrete.

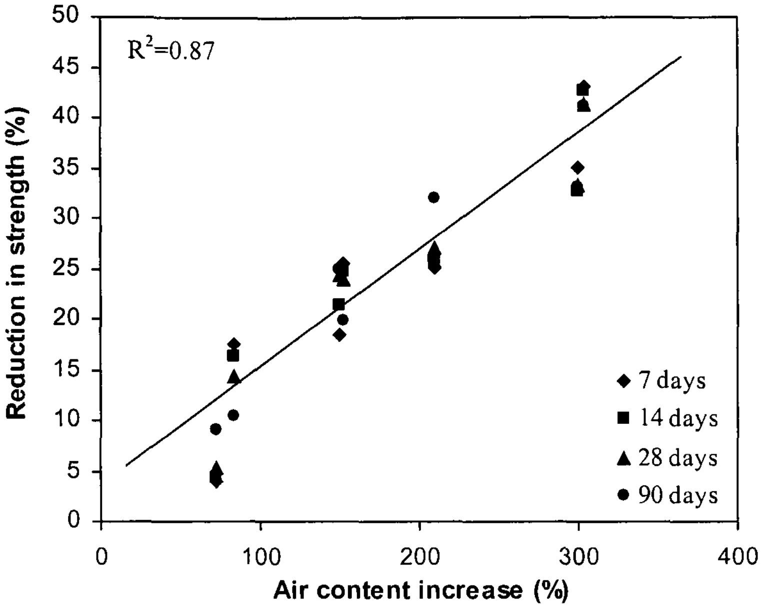


Figure 4.16 Percentage strength reduction versus percentage air content increase for concretes under investigation at different curing ages.

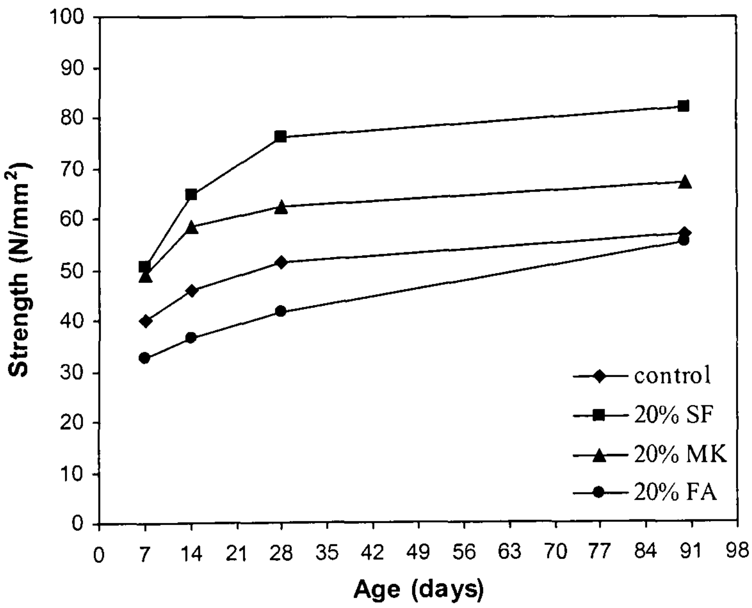


Figure 4.17 Effect of SF, MK and FA on the compressive strength development of concrete at 20% cement replacement.

the strength of SF concrete is significantly greater at extended ages than that of the control, MK and FA concretes. As expected SF and MK concretes achieve strengths in excess of the control whereas FA concrete showed lower strengths than the control.

Figure 4.18 gives the development of compressive strength with age for concretes containing various levels of the three pozzolans with similar air contents. The rate at which strength develops varies considerably for the different concretes. At 7 days the strengths of the SF concrete are very similar to those of the equivalent MK concretes and significantly greater than the control. However the rate of increase in strength from 7 to 28 days is much greater for the SF concrete than for the MK concrete particularly at 20% replacement. Also beyond 28 days the 20% SF concrete still continues to gain strength at a greater rate than the control which is not the case for the MK concrete. In fact beyond 14 days the MK concretes both at the 10 and 20% replacement levels gain strength at a slower rate than the control. Thus MK concrete only provides strength enhancement up to 14 days, and beyond 14 days the effect of that enhancement is diminished whereas for SF concrete, particularly at high levels of replacement (20%), strength enhancement, although very considerable at 14 days still continues up to 90 days. For FA concrete strengths are substantially retarded at 7 days, particularly as the FA content increases. Between 7 and 28 days the rate of strength development is very similar to the control for all compositions. However between 28 and 90 days the rate of strength development for all the FA concretes is greater than the control, therefore as curing time increases there is a tendency for the FA concrete strengths to converge with that of the control. This comparison highlights clearly the distinct differences between the effects of these three pozzolans on concrete strength development which are a result of the differences in both their chemical and physical make up.

Figure 4.19 shows the strength as a function of age for the control concrete and concretes containing FA-MK blends of various proportions. The concretes represented in this figure had air contents ranging from 2.3 to 3.2%. An important feature to note is the consistency of performance with regard to blend compositions

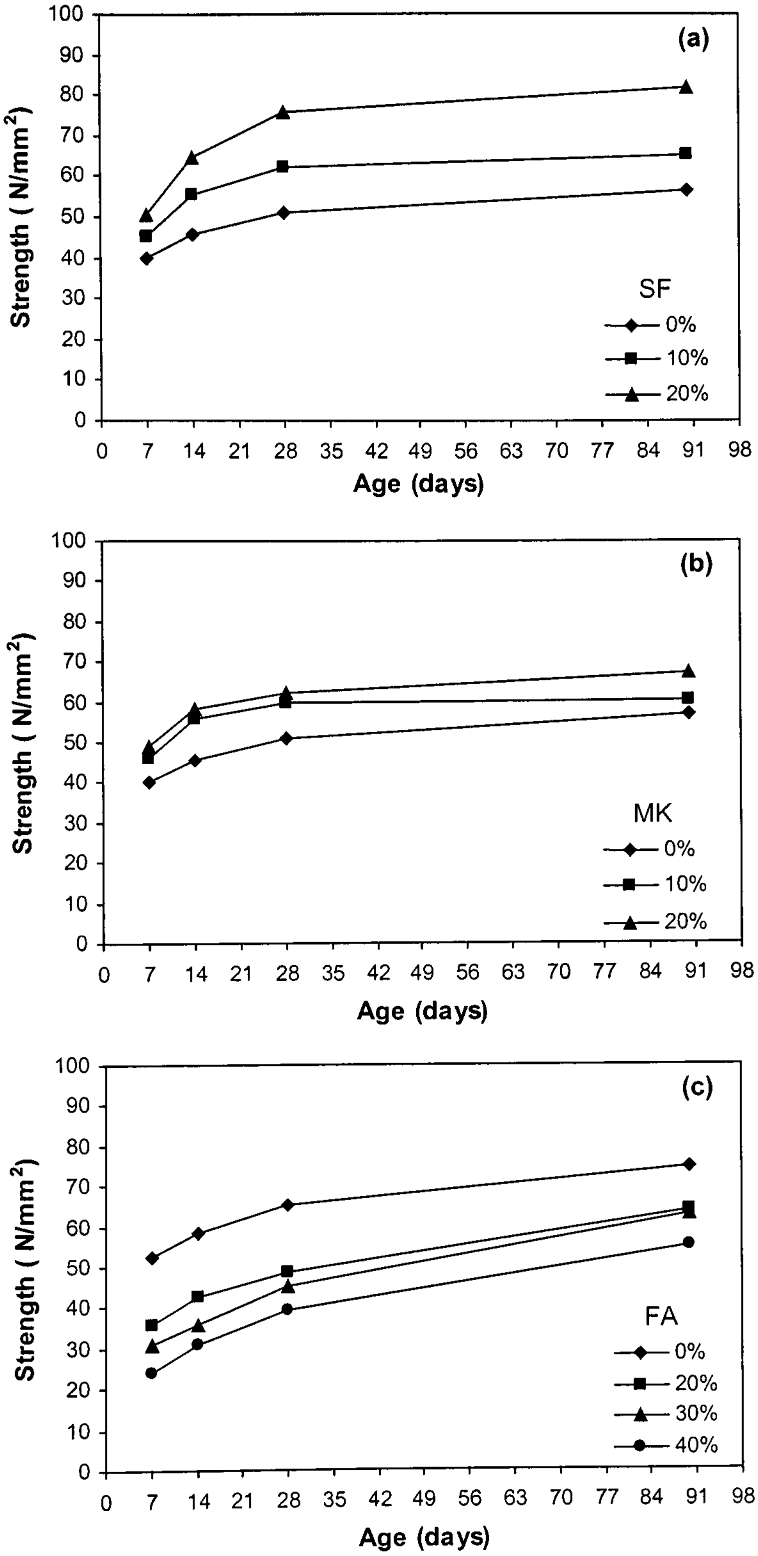


Figure 4.18 Effect of (a) SF (b) MK (c) FA on the compressive strength development for different cement replacement levels.

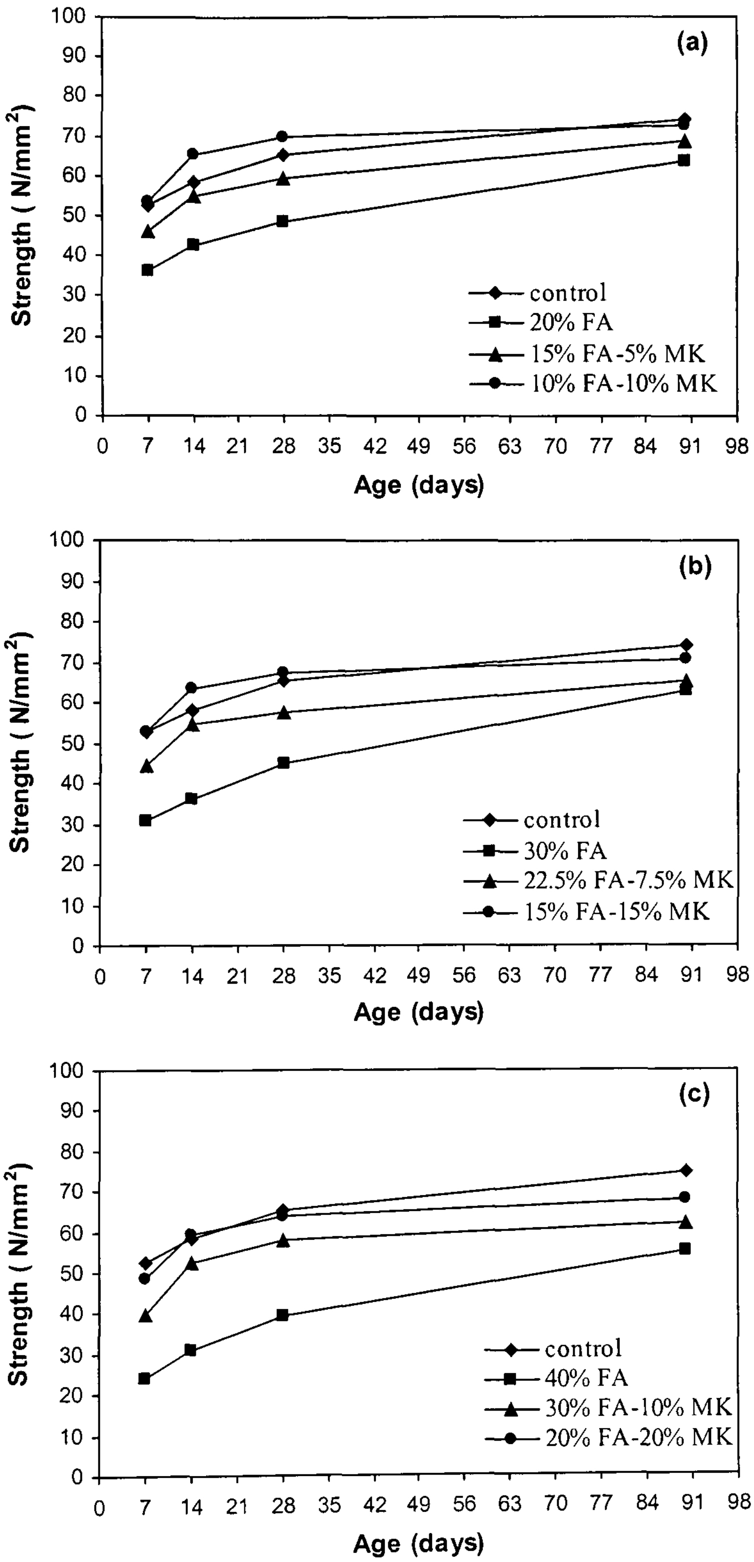


Figure 4.19 Effect of FA-MK blend on the compressive strength development at (a) 20% (b) 30% and (c) 40% total cement replacement.

for all total replacement levels, i.e. 20, 30 and 40% (Figures 4.19(a)-(c)). In general irrespective of the total cement replacement level the strength increases as the MK content increases at all ages. It can be seen that when the cement in the control concrete is partially replaced by 20% FA (Figure 4.19(a)) considerable reductions in strength take place. However, the strength increases significantly when 5% of the FA is substituted by MK. The addition of 5% MK results in recovery of most of the strength lost due to the addition of FA, particularly at the early stages of curing (7-28 days). Further blending with MK, results in strengths which are in excess of the control at the early stages of curing and very nearly equal to the control at 90 days. Similar behaviours to those just described for 20% total cement replacement were observed for 30 and 40% total cement replacement as shown in Figures 4.19(b) and (c) respectively. In all cases, the strength at 90 days was lower than that observed for the control concrete, suggesting that FA would act at greater ages to develop strengths in excess of the control. On comparison of the results for the three total replacement levels it is clearly seen that the greater the replacement level, the greater the reductions in strength relative to the control. This is because of the slow pozzolanic reactivity of the FA which produces considerable reductions in the strength particularly at early ages.

4.3 Concluding remarks

From the work described in this chapter it was found that for given slump and air content, SF has more demand for superplasticiser and air-entraining admixtures than MK. There was also evidence to suggest that the superplasticiser enhances the performance of the air entraining admixture and/or itself plays a secondary role in entraining air within the fresh concrete.

A three fold increase in slump is produced in control and 10% SF concretes by adding 0.12% of air entraining admixture. Although further additions of the admixture lead to increased slump in the control, little benefit in workability is exhibited by the SF concrete. This is attributed to the greater diffusion of the air entraining agent and consequent adsorption of the admixture by the very fine SF particles. The increase in workability attributed to the air entraining admixture is greater in MK concrete than in SF concrete. Also the improvement in workability of MK concrete occurs for a greater range of dosages of the admixture. This is attributed to the smaller specific surface of MK with less of the admixture being adsorbed. In the case of FA concrete the increase in slump due to the air-entraining admixture (up to 0.18%) occurs only in concretes with low levels of FA (20%). Concretes with 30 and 40% FA, although more workable, accrue no such benefit. Non air-entrained control, SF and MK concretes all have the same volume of naturally entrapped air (approximately 2%). This is attributed to the role played by the additional superplasticiser used in the SF and MK concretes. The workability of FA-MK concrete is substantially reduced with increasing MK level at all total replacement levels, 20, 30 and 40%.

As far as the effect of air entrainment on air content of fresh concrete, it was found that up to 0.12% air entraining admixture results in steep rises in the air content of superplasticised SF concrete. The benefits of higher levels of the admixture diminish, particularly in concretes with high SF contents (20%). Compared to the limit of 0.12% for SF concrete, up to 0.24% air entraining admixture results in a steady increase in the air content of MK concrete. On the other hand, FA causes large reductions in the air content of fresh concrete, irrespective of the dosage of the air entraining admixture.

The compressive strength of all concretes show systematic and generally linear reductions with increasing air contents (2 to 10%) of the fresh concrete. The 20% FA concrete resulted in reduced strengths at all stages up to 90 days at which time the strength was approximately the same as that of the control. At all ages 20% SF and 20% MK concretes gave strengths which were considerably greater than those of the control. SF exhibited a greater influence on strength than did MK throughout the 90 day curing period and beyond 14 days the rate of strength development of MK concrete is less than that of the control. SF and MK concretes show significant increases in compressive strength up to 14 days and the SF concrete beyond 14 days. FA concretes exhibited greater potential for increased strength at extended ages than either the SF and MK concretes, although early strength development was severely retarded. These behaviours are attributed to the level and nature of pozzolanic activity which in the case of SF and MK occur in the early stages of curing together with acceleration in cement hydration, compared to the short term "inert" behaviour of FA and the longer term pozzolanic activity. However in contrast to MK, SF also shows some long term pozzolanic activity. Finally, considerable enhancement in compressive strength is achieved in the short and long terms when MK replaces part of the FA. Greater increases in the strength are obtained with increasing MK to FA ratios.

Chapter 5 – Freeze-thaw durability and air void characteristics

Part of this chapter describes the mathematical expressions used for the evaluation of freeze-thaw performance, explains how the air void parameters are calculated based on ASTM C457 and outlines the limitations and assumptions on which these calculations are based. The main body of the chapter deals with the freeze-thaw performance of the air-entrained and non air-entrained concretes investigated. The durability factor, expansion, and pulse velocity measurements together with weight loss measurements are used to evaluate this performance. The results from the optical microscopy work are also presented in an attempt to investigate the effect of the different mineral admixtures on them and to establish possible relationships between the mineral admixtures and freeze-thaw performance.

5.1 Evaluation of freeze-thaw performance

The main process of damage in a freeze-thaw environment involves internal deterioration and surface scaling. These forms of deterioration of concrete can be assessed in several ways. The most common method is to measure the change in the dynamic modulus of elasticity of the specimen, the reduction in which after a number of cycles of freezing and thawing, gives a measure of the resulting internal damage. The relative dynamic modulus of elasticity E_r is determined from:

$$E_{r,c} = \left(\frac{n_1}{n} \right)^2 \times 100 \qquad [5.1]$$

where $E_{r,c}$ is the relative dynamic modulus of elasticity after c cycles of freezing and thawing (as a percentage); n_1 is the fundamental frequency after c cycles of freezing and thawing; and n is the fundamental resonant frequency before freezing and thawing.

With the ASTM C666 method it is usual to assess the freeze-thaw durability by means of a durability factor (DF). The DF is determined from the relative dynamic modulus of elasticity using the following expression:

$$DF = E_r N / M \qquad [5.2]$$

where E_r is the relative dynamic modulus of elasticity at N cycles (as a percentage); N is the number of cycles at which E_r reaches the specified minimum value for discontinuing the test or the specified number of cycles at which the exposure is to be terminated, whichever is the smaller; and M is the specified number of cycles at which the exposure is to be terminated. The above calculation for the relative dynamic modulus of elasticity and consequently the DF is based on the assumption that the weight and dimensions of the specimen remain constant throughout the test. The resonant frequency is a function of the mass of the concrete specimen, i.e. heavier specimens have a higher frequency. Thus, the loss of weight due to surface scaling leads to a lower frequency, and then, to a smaller DF.

There are no established criteria for acceptance or rejection of concrete in terms of the DF; its value is thus primarily used for comparison of concretes of different formulations. However some guidance in interpretation can be obtained from the following: a factor smaller than 40 means that the concrete is probably unsatisfactory, 40 to 60 is the range for concretes with doubtful performance, above 60, the concrete is probably satisfactory, and around 100 the concrete can be expected to suffer no damage due to freezing and thawing.

The measurement in the change in ultrasonic pulse velocity is another non-destructive method for evaluating the frost resistance of concrete. In this method ultrasonic pulses emitted by a transducer attached at one end of the specimen are transmitted through the concrete and received by another transducer at the other end.

The transit time of the first pulse arriving at the receiver is precisely measured by electronic means as described in BS 1881: Part 203 [1986]. The pulse velocity is calculated by dividing the path length over the transit time as shown below:

$$v_c = L_c / T_c \qquad [5.3]$$

where v_c, L_c and T_c are the pulse velocity, length of specimen and transit time at c cycles, respectively. Although there are three alternative arrangements for placing the transducers in ultrasonic velocity measurement, the direct transmission: transducers placed on opposite concrete surfaces, was followed in this study. Measurement of pulse velocity may be influenced by the test conditions such as the path length, the lateral dimensions of specimen, smoothness of surface and the moisture content of concrete [Chung and Law, 1983]. In addition it was reported by Swamy and Darwish [1998] that the presence of pozzolans like FA, SF or combination of the two has little effect on pulse velocity

The effects of freezing and thawing can also be assessed from the loss of compressive or flexural strength or from observations of the change in length or in the mass of the specimen. Although it is described as an optional procedure by the ASTM C666 standard, the length change of concrete specimens is generally considered as the most sensitive index of internal microcracking due to freezing and thawing and its measurement is the only means of assessment used in BS 5075: Part 2 [1982]. A large change in length is an indication of internal microcracking: a value of 200 μm/m for tests in water is taken to represent serious damage [Foy et al., 1988]. The length change is given by:

$$\varepsilon_n = (L_n - L_0)/L_0 \qquad [5.4]$$

where ε_n is the length change after n cycles of freezing and thawing, L_n is the length between the two length gauge inserts on the concrete specimen after n cycles of freezing and thawing and L_0 is the initial length. The precision of this measurement is usually 10 μm/m approximately.

5.2 Calculation of air-void system parameters

The basic characteristics of the air-void system such as the air content, the specific surface and particularly the spacing factor, cannot be measured in a three dimensional volume. Fortunately, thanks to stereology, the magnitudes of these microstructural features can be estimated from their projection on a planar surface. There are three methods of obtaining the data in a strereological model, as illustrated in Figure 5.1. The technique used in this study was the modified point count method. In this method, observations are made over a net of discrete points regularly distributed along lines of a traverse across the entire surface. Essentially the method consists of following with the crosshairs of the microscope the traverse lines and recording the number of voids intercepted (N_v), the total number of point counts (S_t), the number of point counts over an air void (S_v) and over cement paste (S_p).

The ASTM C457 Standard gives the mathematical equations necessary to compute the characteristics of the air-void system from the measured point counts. The air content (A) corresponds to the volume occupied by the air void expressed as a percentage of the total volume of hardened concrete. It is given by the ratio of the surface occupied by the air voids (S_v) to the total surface examined (S_t) under the microscope.

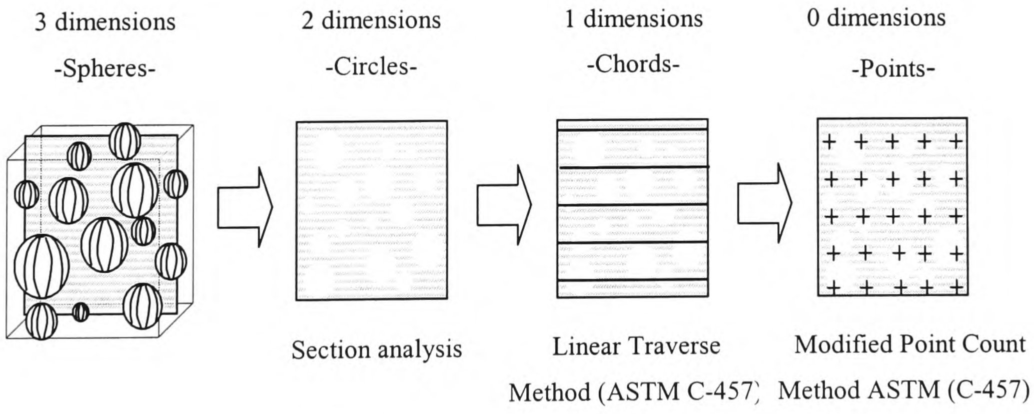


Figure 5.1 Schematic description of the three different methods used in order to assess the characteristics of air-void system in hardened concrete [after Pleau et al., 2001].

Thus: $A = \frac{S_v}{S_t} \times 100$ [5.5]

The specific surface of air voids (α) is defined as the ratio between the surface area of air voids and the total volume occupied by these voids. It can be obtained from the following relationship:

$$\alpha = \frac{4N_V}{S_v I} \quad [5.6]$$

where I is the distance between the regularly spaced points. The specific surface is a function of the mean size of the air voids: larger values of α correspond to smaller air voids. It typically ranges from about 10 mm^{-1} for non air-entrained concretes to more than 40 mm $^{-1}$ for air-entrained concretes.

The efficiency of the air-void system created by air entrainment is governed by the spacing of the air voids which determines the maximum distance that freezing water must travel to reach an escape boundary. The spacing factor, denoted as $\bar{L}$, is defined as half the average distance between the outer boundaries of two adjacent air voids. According to the definition of the ASTM C457 Standard test method, the spacing factor is given by the following relationships:

$$\bar{L} = \frac{S_p I}{4N_V} \text{ when } p/A \leq 4.34, \quad [5.7]$$

$$\bar{L} = \frac{3}{\alpha}\left[1.4\left(\frac{p}{A}+1\right)^{1/3} - 1\right] \text{ when } p/A > 4.34 \quad [5.8]$$

where p represents the paste content expressed as a fraction of the total volume of concrete.

Thus $p = \frac{S_p}{S_t} \times 100$. [5.9]

It should be mentioned here that $\overline{L}$ is computed assuming that all the air voids are equal in size and are regularly spaced in a cubic arrangement as shown in Figure 5.2. Consequently, it can be demonstrated that the spacing factor only provides a rough index, which always overestimates the real spacing of the air voids.

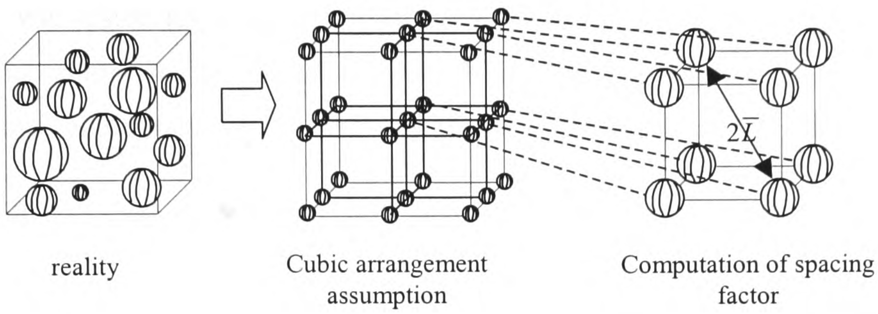


Figure 5.2 Schematic description of the simplifying assumptions used in the computation of the ASTM C457 spacing factor [after Pleau et al., 2001].

5.3 Results and discussion (series 1)

Freeze-thaw testing was initially based on BS 5075: Part 2 which stipulates one cycle of freezing and thawing per 24 hours. The temperatures were continuously monitored using thermocouples. Figure 5.3 depicts typical temperature profiles in the chamber, container water and the centre of specimen over a 24-hour period.

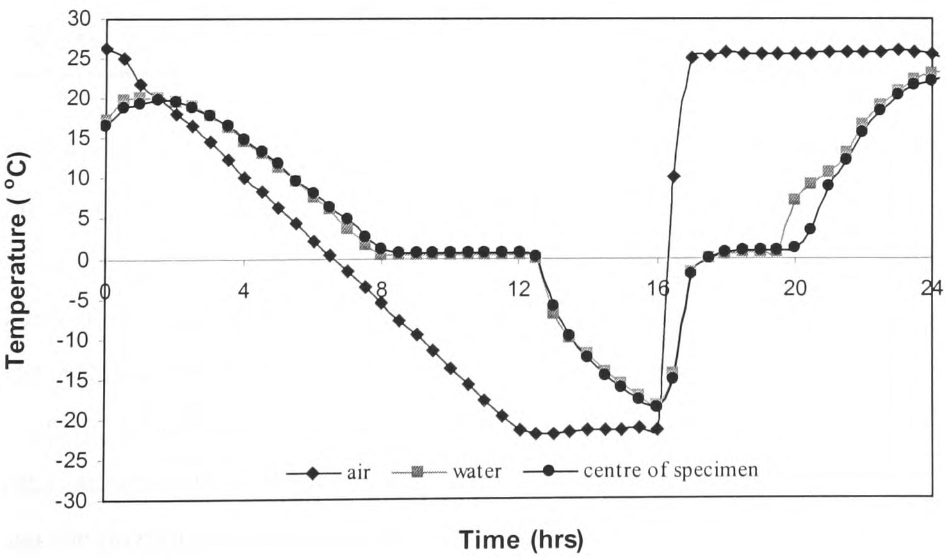


Figure 5.3 Typical freezing and thawing cycle used for concretes in series 1.

It can be seen that the temperatures at the centre of the specimen vary between approximately –18°C and +22°C, which is within the range stipulated in BS 5075. The test specimens comprised samples from the control concrete and concretes incorporating SF, MK or blends of FA and MK at 10% total PC replacement. The fresh concrete was subjected to slump and air content tests while the hardened concrete was tested for compressive strength at 7, 14, 21 and 28 days. Freeze-thaw data which comprised the resonant frequency, durability factor, pulse velocity and weight loss can be found in Tables B.1 to B.4 in Appendix B.

5.3.1 Slump, air content and compressive strength

The results of the slump, air content and compressive strength are given in Table 5.1. All the concretes were air-entrained and devised to have around 6 ± 1% air. The slumps varied between 95and 130 mm.

Table 5.1 Slump air content and compressive strength development for concretes in series 1.

Mix ref.	*Slump (mm)*	*Air content (%)*	*Compressive strength (N/mm^2)*			
			7 days	*14 days*	*21 days*	*28 days*
CON 20/12	130	7.0	17.9	20.5	23.2	24.6
10S 30/12	95	5.5	27.8	36.8	43.9	45.1
10M 30/12	95	5.6	31.6	38.3	40.2	41.2
7.5F2.5M 20/18	110	5.3	16.3	19.1	19.8	20.3

Figure 5.4 shows a comparison of the compressive strength of the concretes at 7, 14, 21 and 28 days. At all curing times partial replacement of PC by 10% SF or MK results in significant increases in compressive strength whereas the replacement by 7.5% FA blended with 2.5% MK leads to small reductions. The results also show that the pozzolanic activity of MK is greatest at early stages of curing (7-14 days) after which a levelling off in strength occurs. Both PC-MK and PC-MK-FA concretes achieve 93% of the ultimate strength (at 28 days) after 14 days curing. In contrast the pozzolanic activity of SF continues beyond 14 days.

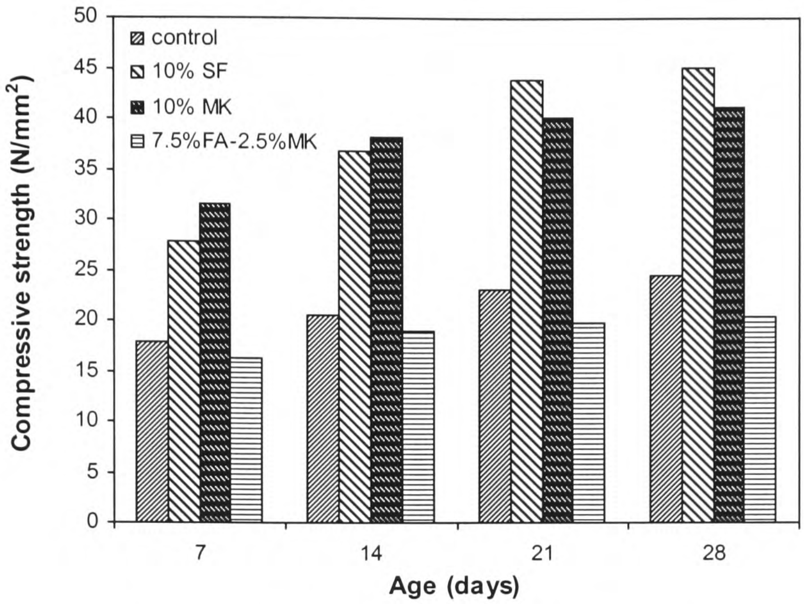


Figure 5.4 Strength development for concretes tested in series 1

5.3.2 Freeze-thaw performance

The durability factors, expansion and pulse velocity data for up to 124 cycles of freezing and thawing are shown in Figure 5.5. Considerable deterioration takes place in the control concrete after about 60 cycles. The concretes containing pozzolans, however, show insignificant changes in durability factors and pulse velocities. Although some expansion takes place in the pozzolan concretes as the number of cycles increases particularly in the SF concrete (Figure 5.5(b)), in general these specimens indicate insignificant internal deterioration caused by freezing and thawing action. Furthermore, there are no marked differences between the performance of the specimens containing the different pozzolans.

Figure 5.6 gives the results for the weight loss in both the BS 5075 and ASTM C666 specimens due to freezing and thawing for up to 124 cycles. Both specimens show that considerable reductions in weight loss occur when pozzolans are employed. The best performance is exhibited by the concrete with 10% MK followed by 10% SF and the ternary FA-MK blend concrete. Visual inspection revealed that there was less

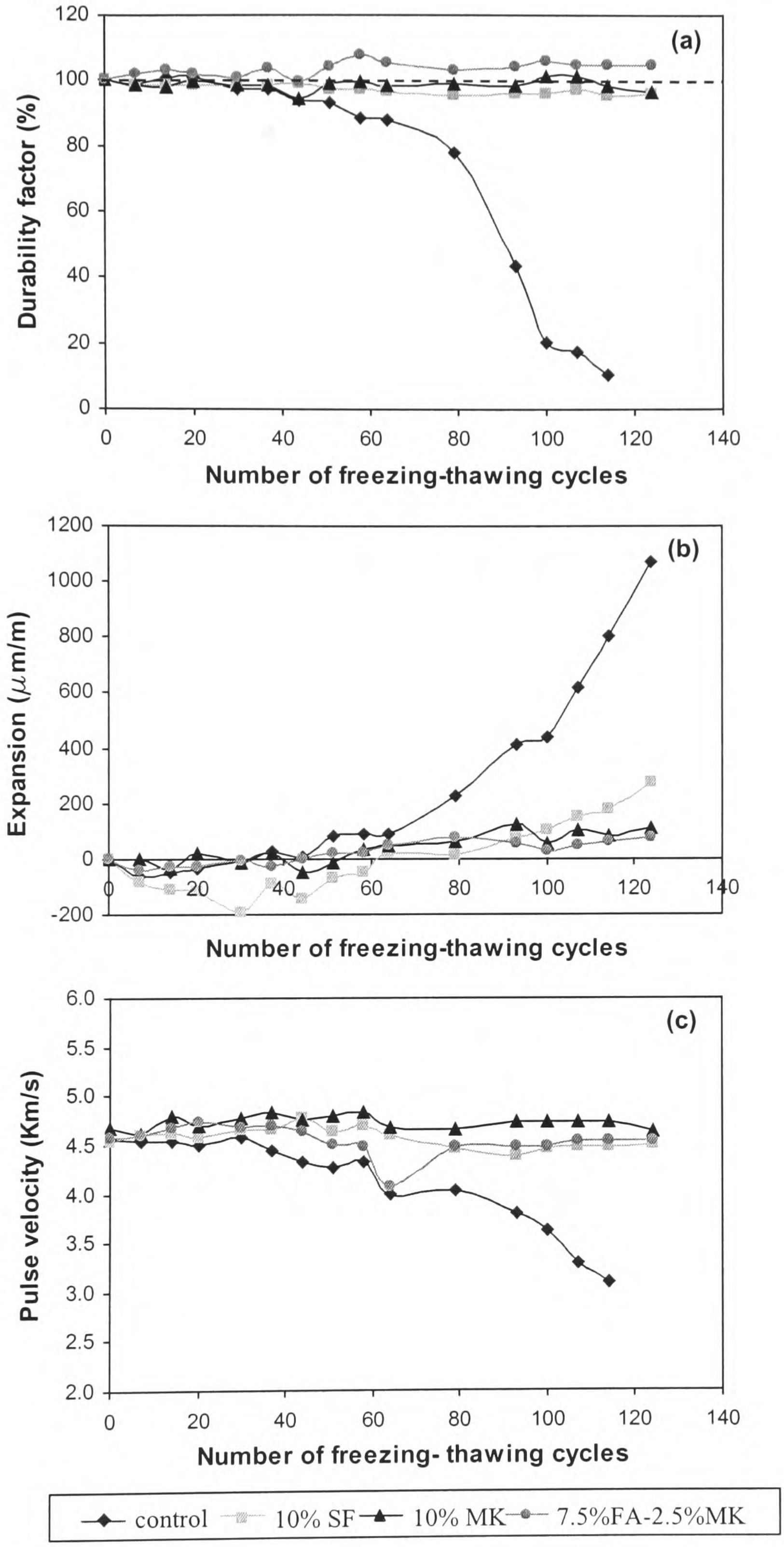


Figure 5.5 Influence of pozzolans on (a) durability factor (b) expansion and (c) pulse velocity of air-entrained concretes used in series 1.

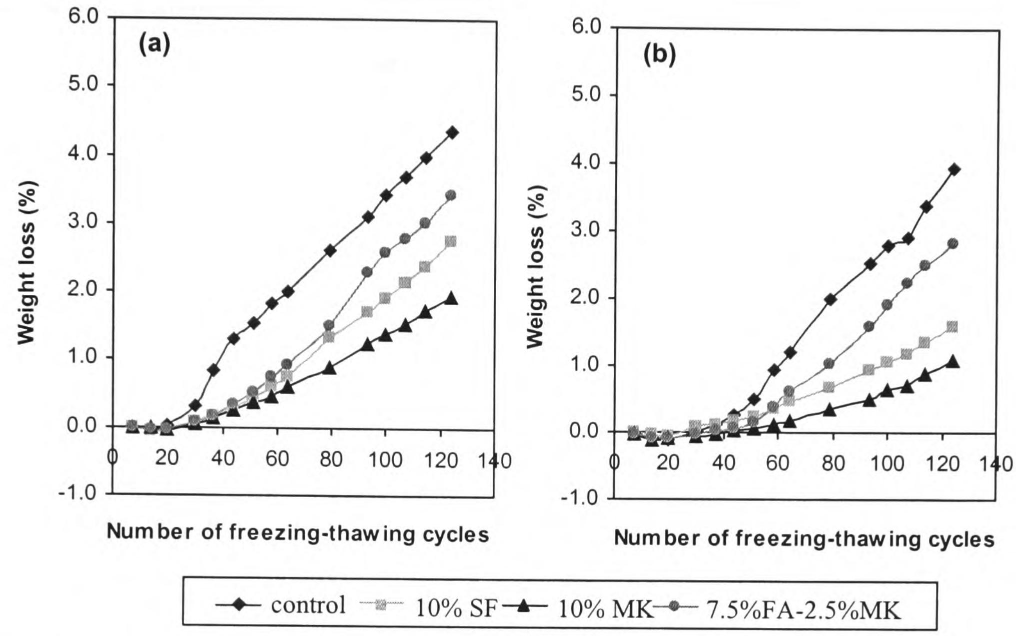


Figure 5.6 Influence of pozzolans, on weight loss of (a) BS 5075 and (b) ASTM C666 specimens used in series 1.

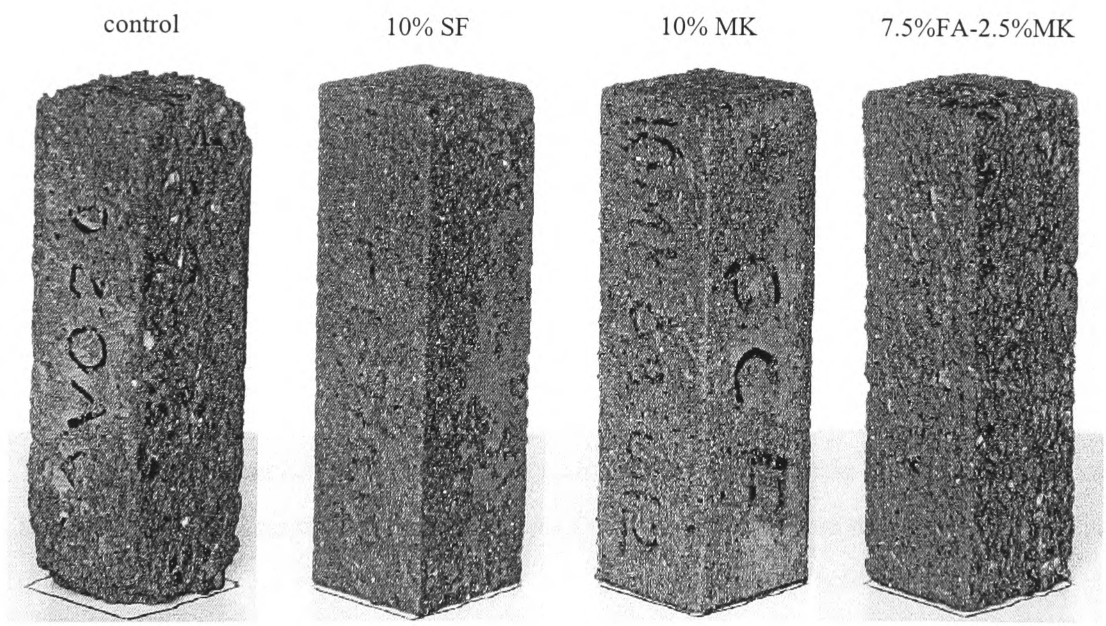


Figure 5.7 Condition of ASTM C666 series 1 specimens after 124 cycles of freezing and thawing.

scaling on the surfaces of the specimens containing pozzolans at the end of freeze-thaw testing as shown in Figure 5.7.

Table 5.2 gives the results for the compressive strengths before and after 124 cycles of freezing and thawing. The compressive strengths at 21 days, prior to freezing and thawing, were obtained using 100 mm cubes whereas the strengths after freezing and thawing were obtained from the prisms (cross section 75 mm x 75 mm) using the equivalent cube test in accordance with BS 1881: Part 119 [1983]. In view of the size differences a direct comparison between the results could not be made and the data were adjusted using the results of a separate study described in Appendix C. The data shown in Table 5.2 take account of the necessary adjustments. The results confirmed the poor freeze-thaw performance of the control concrete, which exhibited high reduction in strength and low flexural strength, and the good performance of the other concretes, which showed insignificant changes in compressive strength and high values of flexural strength.

Table 5.2 Compressive and flexural strengths of concretes in series 1 after 124 cycles of freezing and thawing.

Concrete	*Compressive strength (N/mm^2)*		*Loss of strength (%)*	*Flexural strength At 124 cycles (N/mm^2)*
	At 21 days	*At 124 cycles*		
Control	23.2	11.3	51	1.3
10% SF	43.9	42.6	3	4.0
10% MK	40.2	41.1	-2	4.8
7.5% FA-2.5% MK	19.8	19.2	3	4.1

The air void characteristics of the concretes presented in Table 5.3 do not provide any indication of the reason behind the poor performance of the control concrete. On the contrary the control concrete had the lowest spacing factor (229 μm) which should give better freeze-thaw performance.

In general, the above results show that all concretes containing pozzolans give good performance under freezing and thawing. In the next series of tests it was decided to follow a more severe freezing and thawing regime using both air-entrained and non air-entrained concretes, in an attempt to reveal differences in performance due to the incorporation of different pozzolans.

Table 5.3 Air void characteristics for concretes in series 1.

Concrete	A_{hard} (%)	*n* (per mm)	*p* (%)	α (mm^{-1})	$\bar{L}$ (μm)
Control	6.8	0.22	20.2	13.0	229
10% SF	4.9	0.19	20.9	15.4	275
10% MK	4.3	0.19	25.9	17.8	284
7.5% FA-2.5% MK	4.4	0.17	22.1	15.8	294

5.4 Results and discussion (series 2)

The concretes involved in this part of the investigation were subjected to approximately two cycles of freezing and thawing per 24 hours. The temperatures of air in the chamber, container water and inside the specimens over the first 48-hour period for this freeze-thaw regime are shown in Figure 5.8. The temperature at the centre of the specimen varies between approximately –15 to +5°C, which is within

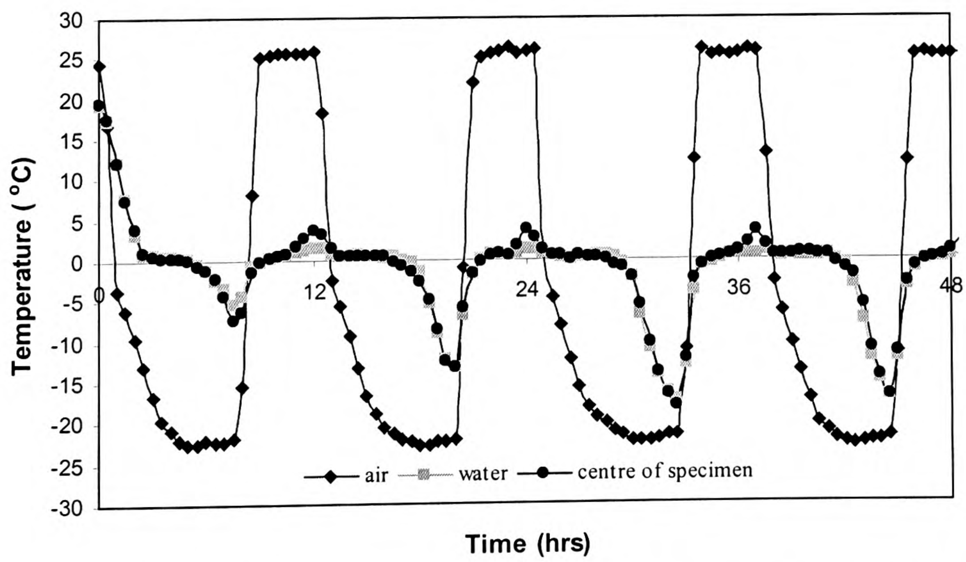


Figure 5.8 Typical freezing and thawing cycle used for concretes in series 2.

the range stipulated in ASTM C666.

The results reported in this section relate to the concrete mixtures, whose details are given in Table 3.6. These comprised non air-entrained and air-entrained mixtures with 0, 2.5, 7.5 and 10% MK and 10, 30% FA. Other mixtures incorporated combinations of FA and MK with blend ratios of FA:MK of 3:1 at 10 and 30% total PC replacement levels. This section gives the results for the fresh concrete properties and compressive strength before and after freezing and thawing. It also gives the DF, expansion, and pulse velocity measurements which with the weight loss measurements were used to evaluate freeze-thaw resistance. The numerical data for this series of concretes are given in Tables B.5 to B.20 in Appendix B.

5.4.1 Slump, air content and compressive strength

The slump, air content and compressive strength development results of these concretes are given in Table 5.4. In the case of air-entrained concrete the mixtures had air contents of 6.5 ± 1.5%. The non air-entrained concretes had air contents of around 2% and slumps of around 100 mm.

Figure 5.9 shows the influence of the level of PC replacement by MK on the compressive strengths. As might be expected, the air-entrained concretes (Figure 5.9(b)) show reduced strengths at all ages as compared to the non air-entrained concretes (Figure 5.9(a)). Also systematic increases in strength are observed at ages greater than 7 days, as the replacement level is increased. The 7 day strengths show negligible change in strength with increasing MK content. This is due to insignificant quantities of CH being liberated by PC hydration for reaction with MK. At 10% replacement, however, the strength at 7 days show significant increases over those of the control concrete. This may be due to the increased level of MK particles for reaction with the available, although somewhat scarce, CH. The observed effects suggest that the pozzolanic activity of MK is greatest at ages between 7 and 21 days.

Table 5.4 Slump air content and compressive strength development for concretes in series 2.

Concrete	Mixture ref.	Slump (mm)	Air content (%)	Compressive strength (N/mm^2)			
				7 days	14 days	21 days	28 days
Non air-entrained control	CON 14/00	75	2.1	25.8	28.2	34.7	34.1
Air-entrained control concrete	CON 18/10	135	7.5	20.2	22.5	24.7	25.2
Non air-entrained MK concrete	2.5M 07/00	75	2.1	25	30.8	32.7	33.7
	7.5M 15/00	90	2.4	26.1	35.5	39.9	40.1
	10M 30/00	85	2.3	29.4	41.7	45.0	45.8
Air-entrained MK concrete	2.5M 07/06	100	5.6	20.2	24.4	25.7	26.9
	7.5M 15/11	110	7.0	19.7	25.8	30.1	31.2
	10M 17/12	115	6.7	22	32.6	35.8	37.8
Non air-entrained FA concrete	10F 05/00	70	2.1	20.8	25.3	29.5	31.8
	30F 03/00	95	1.3	15.7	18.9	21.6	25
Air-entrained FA concrete	10F 05/24	160	7.9	16.3	19.1	19.8	20.3
	30F 04/40	160	6.6	13.2	14.7	17.2	18.8
Non air-entrained FA+MK concrete	7.5F2.5M 07/00	60	2.2	24.2	29.4	33.6	33.5
	22.5F7.5M 04/00	70	1.8	22.3	30.5	34.6	35.1
Air-entrained FA+MK concrete	7.5F2.5M 06/18	125	7.4	19.3	23.8	26.9	27.5
	22.5F7.5M 04/40	110	5.6	18.4	25.3	27	27.6

The variations in the strength of concrete with increasing PC replacement by FA are shown in Figure 5.10. It should be noted that for both replacement levels of 10 and 30%, the strengths at all curing ages are lower than that of the control concrete. In contrast to MK concrete, the strength of FA concrete decreases with increase in FA content at all curing ages. In addition, both the air-entrained and non air-entrained control concretes seem to achieve their maximum strength at the age of 21 days. The concretes containing FA continue to gain strength indicating long-term pozzolanic activity due to FA. As with the MK concretes, the air-entrained FA concretes give significant reductions in strengths over those of the non air-entrained concretes.

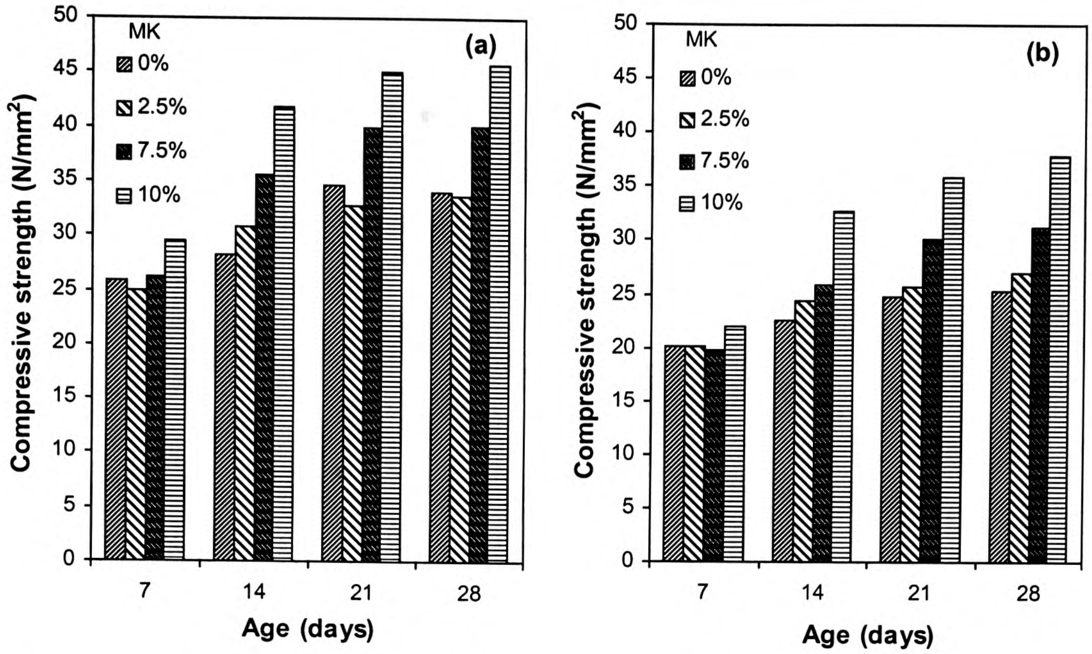


Figure 5.9 Influence of MK on compressive strength development of (a) non-air-entrained and (b) air-entrained concretes.

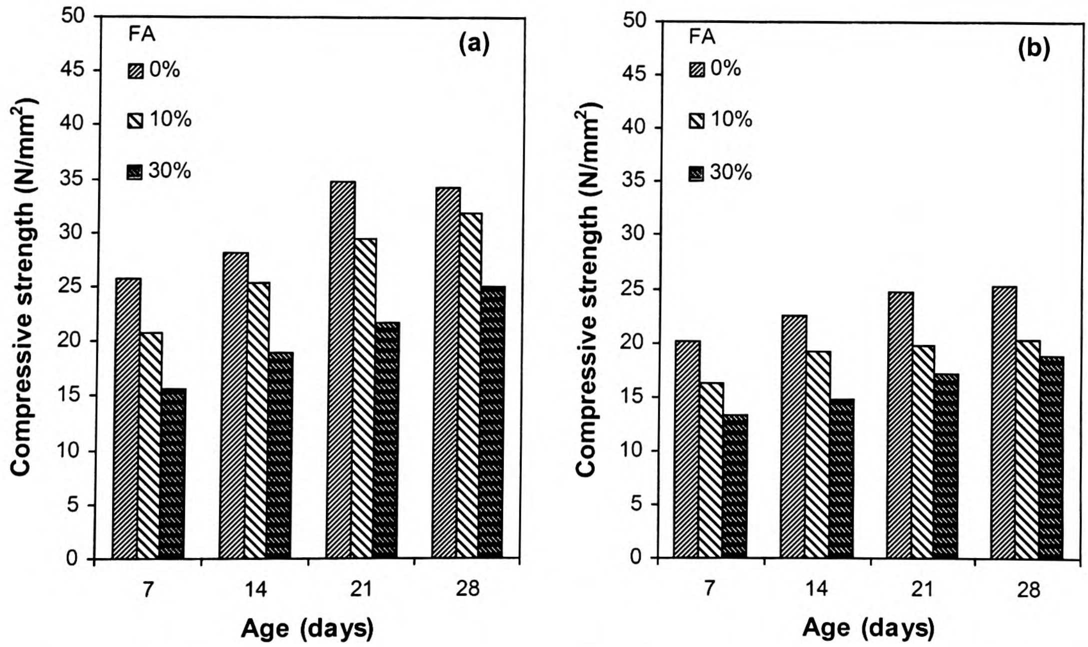


Figure 5.10 Influence of FA on compressive strength development of (a) non air-entrained and (b) air-entrained concretes.

Figure 5.11 compares the strength of the control, 10% FA and 7.5FA+2.5MK concretes at the ages of 7, 14, 21 and 28 days. The distinct feature to note here is that strength recovery, relative to the control, takes place and even strengths in excess of the control are recorded when FA is blended with MK. At the early age of 7 days, possibly due to the slow pozzolanic reaction of FA, the ternary blend (PC-FA-MK) concrete shows inferior strength to that of the control concrete. A similar behaviour by the ternary blend can be observed for concretes with 30% total replacement as shown in Figure 5.12. It is important to note that this performance is maintained at all curing times and for both replacement levels of 10 and 30%. It can therefore be stated that, irrespective of the total replacement level, when the ratio of FA to MK is 3 to 1 the slow development of strength, attributed to FA, disappears and strengths equal to or in excess of that of the control are achieved.

5.4.2 Freeze-thaw performance

Metakaolin concrete

The results of the DF, expansion and pulse velocity during freezing and thawing of non air-entrained MK concrete as compared to the control concrete are shown in Figures 5.13(a)-(c) respectively. The data used to produce these Figures are given in Tables B.5 to B.8. An important feature to note is the consistency of freeze-thaw performance as revealed by all three measurements. Poorest performance is shown by the control concrete where the DF after 80 cycles of freezing and thawing was 15%. This deterioration is further confirmed by the rapid expansion and marked reduction in pulse velocity as shown in Figure 5.13(b) and (c). Although the 10% MK concrete gave somewhat improved performance, the recorded DF and expansion after 120 cycles of freezing and thawing were 16% and 6127 μm/m respectively indicating severe deterioration. The results for the DF indicate greatly improved resistance to freezing and thawing by the concretes with lower MK contents of 2.5 and 7.5%, where the values after 120 cycles were greater than 80% showing satisfactory performance. However, even these concretes performed unsatisfactorily when examined on the basis of the measured expansions. Considering that an expansion of 200 μm/m is an indication of serious damage (see Foy et al., 1988),

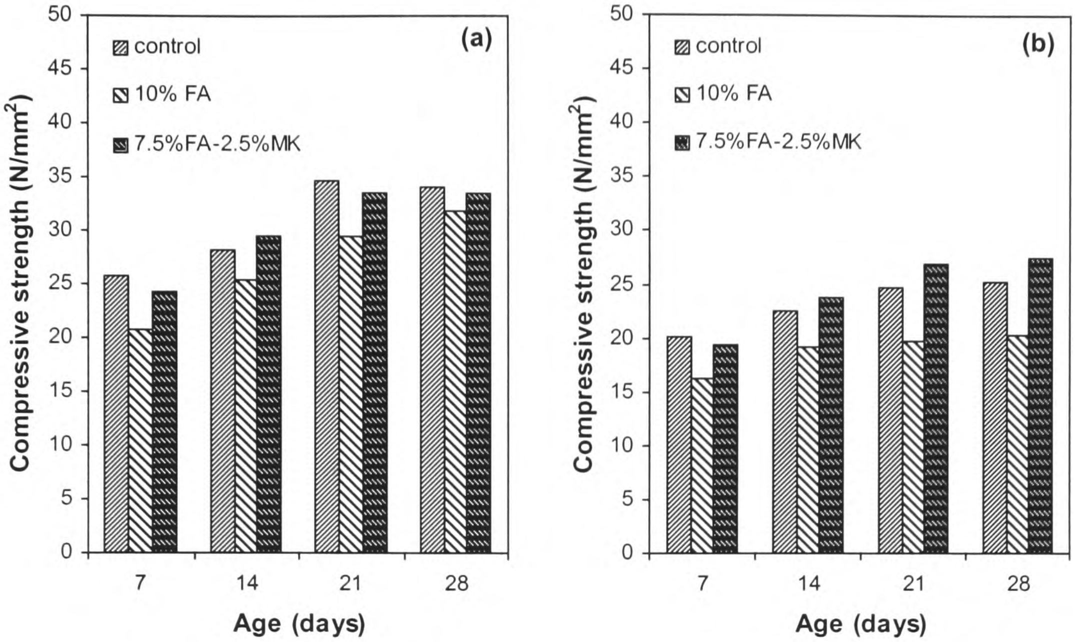


Figure 5.11 Influence of FA-MK blend on compressive strength development of (a) non air-entrained and (b) air-entrained concretes at 10 % total replacement level.

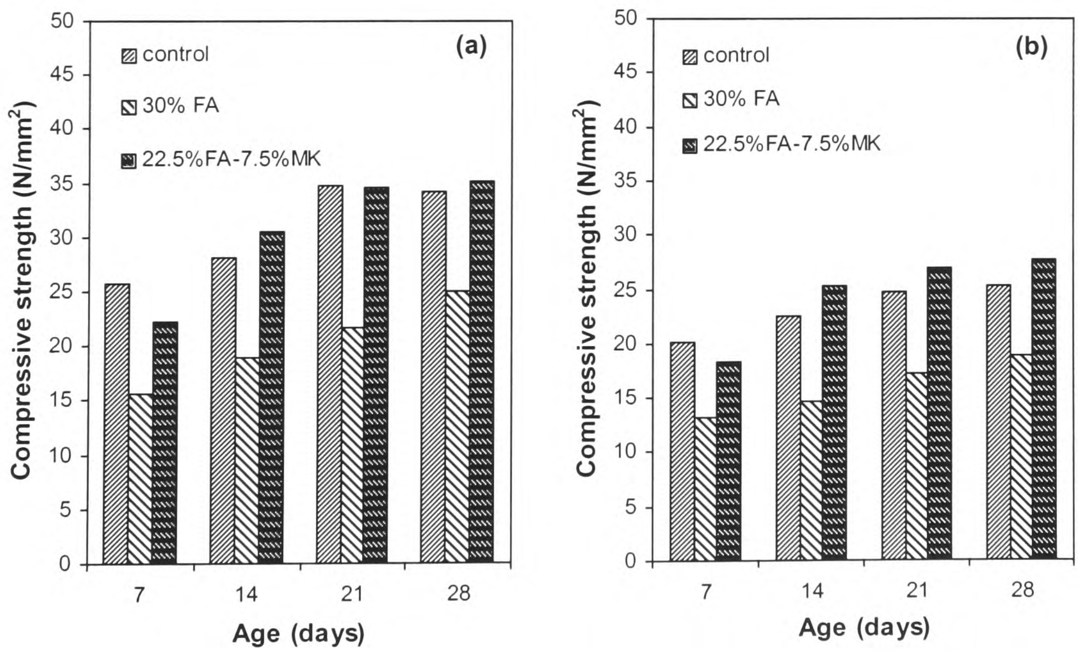


Figure 5.12 Influence of FA-MK blend on compressive strength development of (a) non air-entrained and (b) air-entrained concretes at 30 % total replacement level.

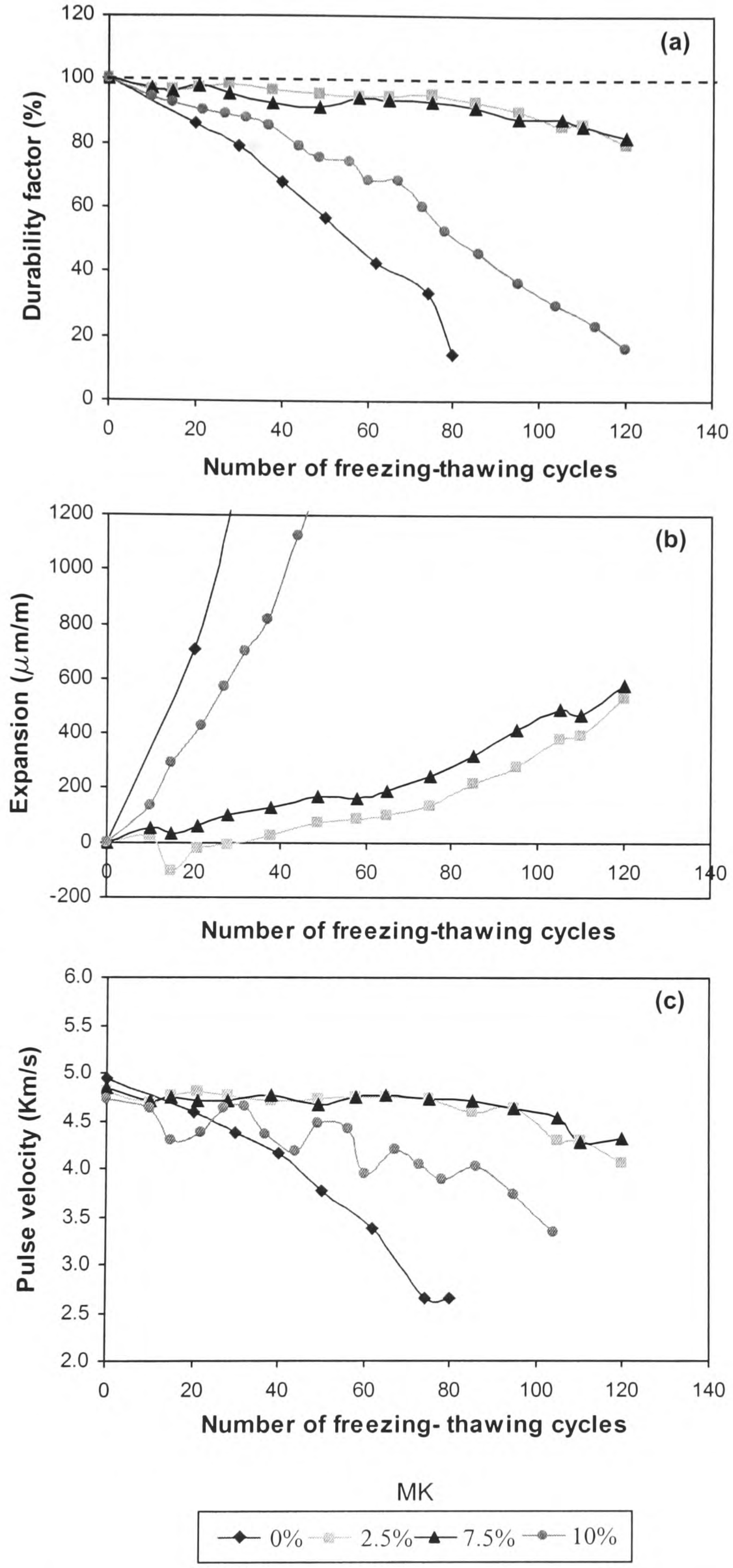


Figure 5.13 Influence of MK on (a) durability factor (b) expansion and (c) pulse velocity of non air-entrained MK concrete.

these concretes exhibit failure after about 80 cycles of freezing and thawing. In fact the measured expansions for these concretes after 120 cycles of freezing and thawing were well in excess of 500 μm/m. It is to be remembered that the test specimens were cured in water for 21 days before being subjected to freezing and thawing. This curing time, although normally found to be sufficient for MK concrete, may not have been long enough to develop full pozzolanic activity to consume all of the MK present at 10% replacement. The unreacted MK particles provide a more porous structure, allowing greater ingress of water and thus causing more internal damage due to the action of freezing and thawing.

The results for the freeze-thaw measurements of the air-entrained specimens are given in Tables B.9 to B.12 and presented graphically in Figure 5.14. It is apparent that the DF, expansion and pulse velocity remained largely unchanged during the 120 cycles of freezing and thawing for all concretes. Not withstanding the similarity of performance of all the concretes, it is interesting to note that the 10% MK concrete showed somewhat more expansion than the control and other MK concretes. This trend, but to a much larger extent, was also shown by the 10% MK concrete (Figure 5.13(b)). Lowest expansion, though not very significant is exhibited by the 7.5% MK concrete. Also, although generally the reduction in pulse velocity due to the action of freezing and thawing is small for all concretes tested, those for the control show relatively significant values (Figure 5.14(c)) indicating some benefit accrued by the incorporation of MK in the system. Figure 5.14(b) also gives some indication of reduced expansions due to the incorporation of 7.5% MK. Although the results shown in Figure 5.14 indicate some benefits attributed to the incorporation of MK, the great improvement in performance over that shown in Figure 5.13 must be attributed to the modification in the air void system characteristics effected by the action of air entrainment. The extent of improvement in this system with respect to resistance to freezing and thawing, is such that it renders the benefits accrued by the MK (see Figure 5.13) to be insignificant, that no obvious effects are displayed. Thus, it would appear that air entrainment is the controlling factor for good freeze-thaw performance and the material effects are less important.

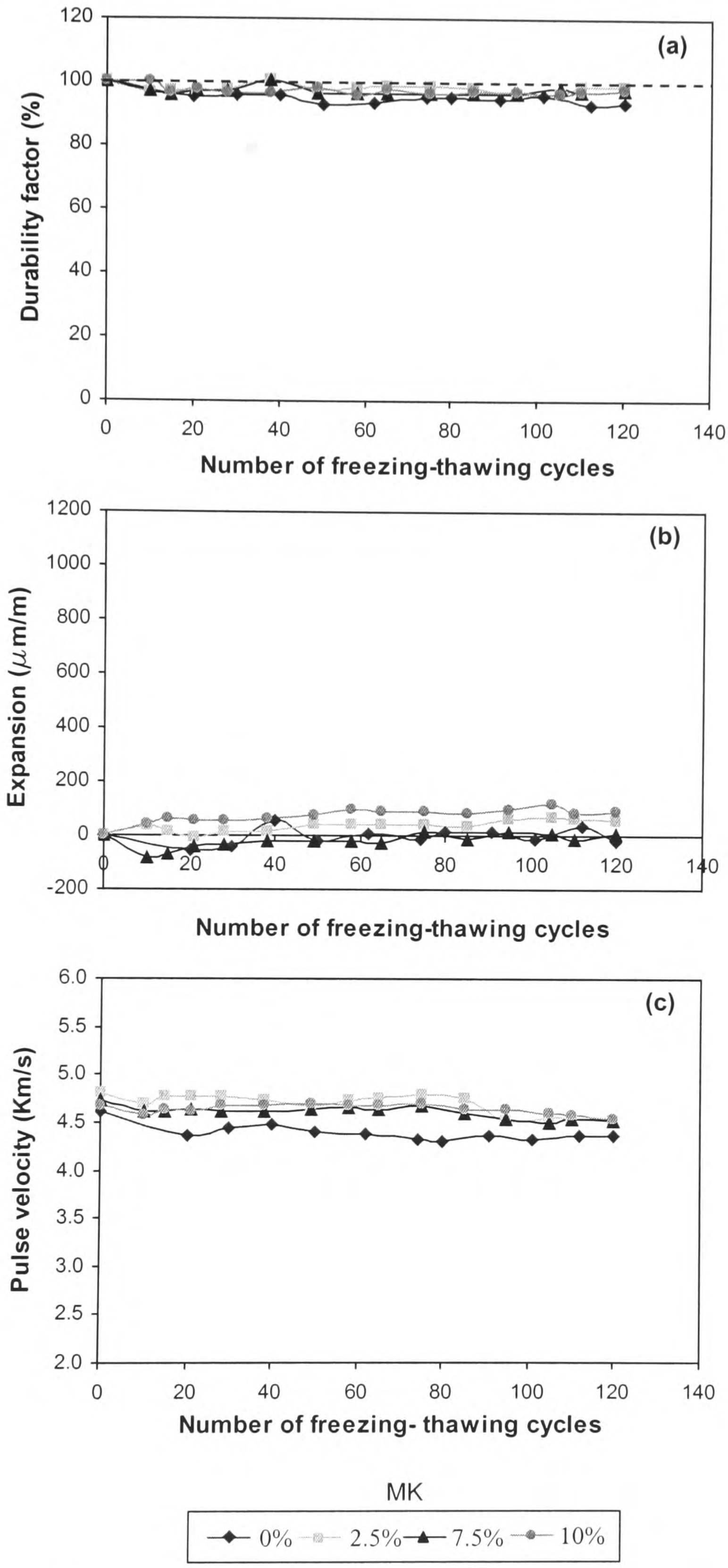


Figure 5.14 Influence of MK on (a) durability factor (b) expansion and (c) pulse velocity of air-entrained MK concrete.

The weight loss of the non air-entrained BS 5075 and ASTM C666 specimens are shown in Figures 5.15(a) and (b) respectively. In both cases it is observed that the weight loss is generally low during the first 60 cycles, irrespective of the MK replacement level. Beyond 60 cycles the control (0% MK) specimens show rapid deterioration indicated by the steep gradients of the weight loss versus number of cycles curves with a weight loss greater than 1% taking place at about 80 cycles of freezing and thawing. Great reductions in weight loss occur when the PC is partially replaced by 2.5% MK giving less than 1% weight loss after 120 cycles. However, the results indicate that further blending with MK leads to increase in weight loss reaching more than 1% at about 100 cycles. Figure 5.16 shows the condition of the ASTM C666 specimens at 120 cycles of freezing and thawing confirming the above observations.

Figure 5.17 gives the results for the weight loss of the air-entrained specimens. On comparison of these results with those shown in Figure 5.15, it is immediately observed that air entrainment leads to dramatic reductions in the weight loss experienced by the specimens. With the exception of the control specimens all MK concretes give weight losses significantly below 1%. An interesting observation is that, contrary to the behaviour shown by the non air-entrained specimens, the weight loss for the air-entrained specimens generally reduces as the MK content increases from 2.5% to 10%. This phenomenon was not displayed by the DF, expansions and pulse velocity measurements (Figure 5.14) where no systematic variations were observed due to the different MK contents. It is to be pointed out that the changes in weight loss due to different MK contents are small and, therefore, could not easily be portrayed by the photographic presentation of the ASTM C666 specimens, after 120 cycles, shown in Figure 5.18.

Table 5.5 gives the results for the compressive strengths before and after 120 cycles of freezing and thawing. The Table also gives the results for the flexural strength at the end of freezing and thawing. The extent of deterioration suffered by the non air-entrained control (0% MK) concrete was such that it was not possible to conduct reliable mechanical tests after 120 cycles of freezing and thawing.

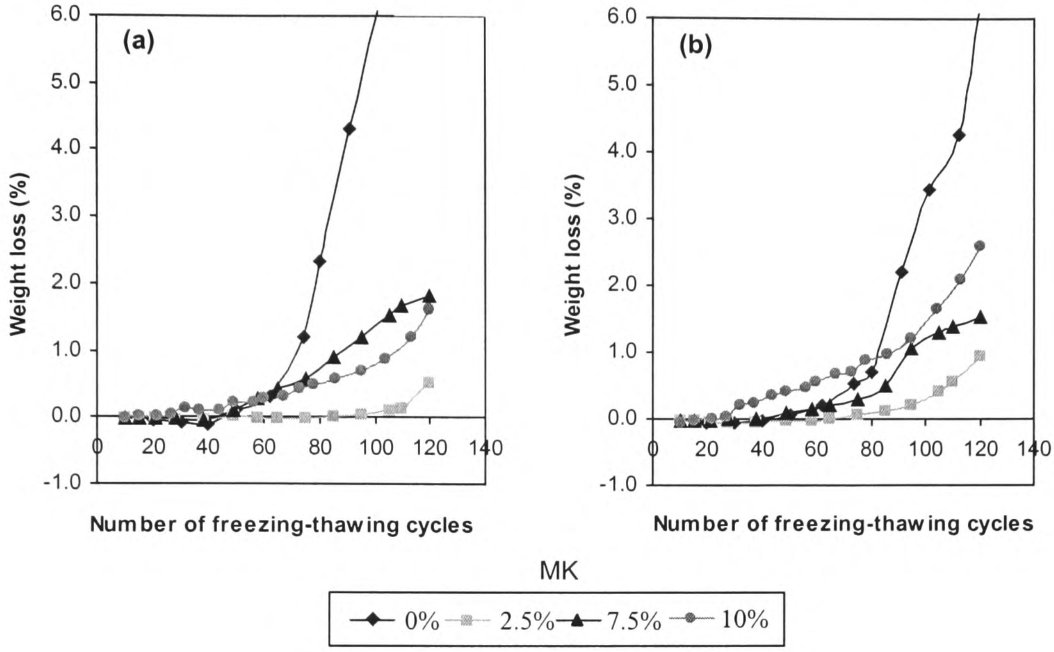


Figure 5.15 Influence of MK on weight loss of non air-entrained concrete for (a) BS 5075 specimen and (b) ASTM C666 specimen.

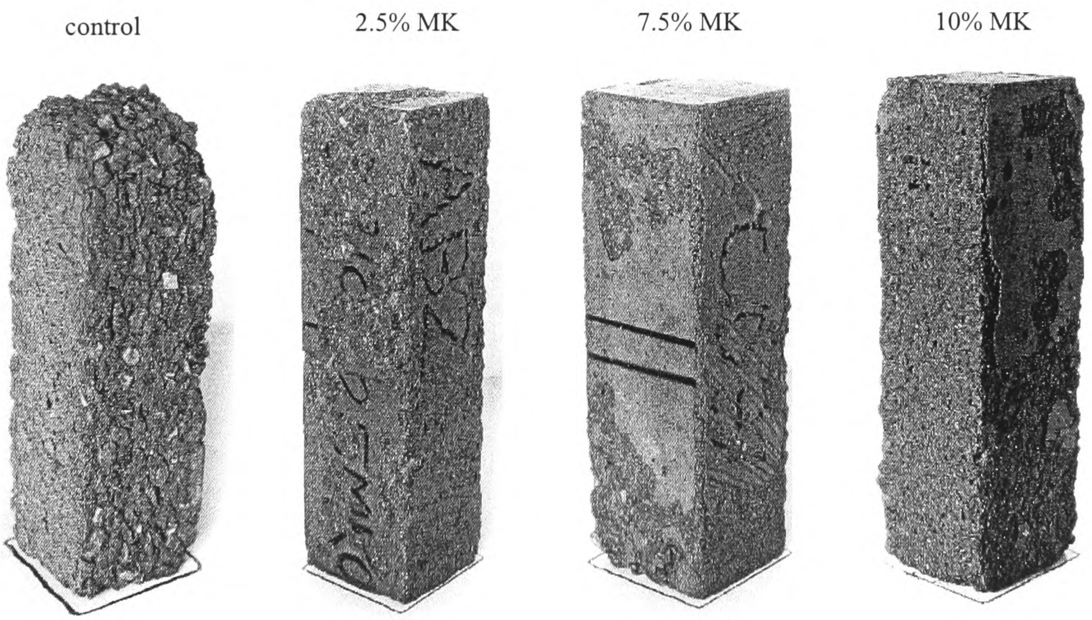


Figure 5.16 Condition of non air-entrained control and MK concrete ASTM C666 series 2 specimens after 120 cycles of freezing and thawing.

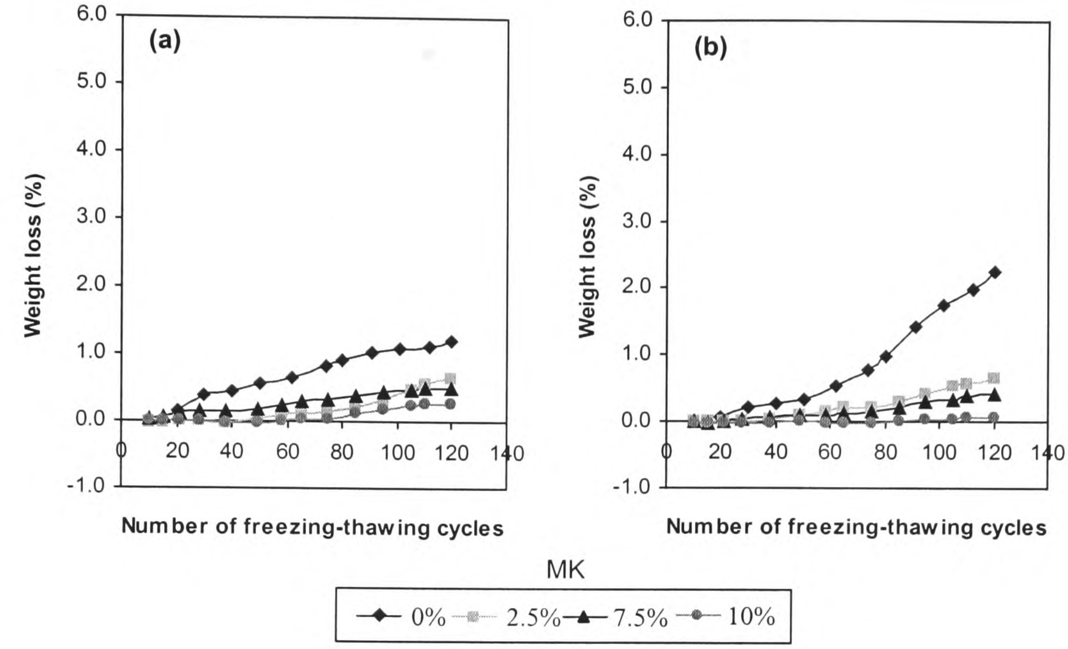


Figure 5.17 Influence of MK on weight loss of air-entrained concrete for (a) BS 5075 specimen and (b) ASTM C666 specimen.

Figure 5.18 Air-entrained control and MK concrete ASTM C666 series 2 specimens after 120 cycles of freezing and thawing.

Table 5.5 Compressive and flexural strengths of MK concrete after 120 cycles of freezing and thawing.

MK content (%)	*Compressive strength* (N/mm^2)		*Loss of strength* (%)	*Flexural strength At 120 cycles* (N/mm^2)
	At 21 days	*At 120 cycles*		
	Non air-entrained			
0	34.7	X	X	X
2.5	32.7	26.3	20	2.9
7.5	39.9	22.7	43	2.4
10	45.0	21.2	53	1.2
	Air-entrained			
0	24.7	20.3	18	4.4
2.5	25.7	28.8	-12	4.6
7.5	30.1	31.3	-4	4.8
10	35.8	34.2	4	4.4

The good performance of the air-entrained MK concrete indicated by the results shown in Figure 5.14 is confirmed by the results for the compressive strength after freezing and thawing. The air-entrained concretes give considerably higher flexural strengths after 120 cycles of freezing and thawing than those of the non air-entrained concretes. Although entrapped or entrained air normally causes strength reductions the results shown in Table 5.5 demonstrate the effectiveness of the entrained air in reducing the internal damage caused by the action of freezing and thawing.

Fly Ash concrete

Figures 5.19(a), (b) and (c) respectively show the changes in the DF, expansion and pulse velocity with increasing number of freezing and thawing cycles for the non air-entrained control and FA concretes. The numerical data for these measurements are given in Tables B.5, B.13 and B.14 in Appendix B. It is evident that the control concrete performed better than concrete where the PC was replaced by 10 or 30% FA. However, all three concretes showed rapid reductions in the values of DFs with a value of less than 60% given by the control concrete after only 50 cycles. Furthermore, the DFs for 10 and 30% FA concrete dropped dramatically to 43% and

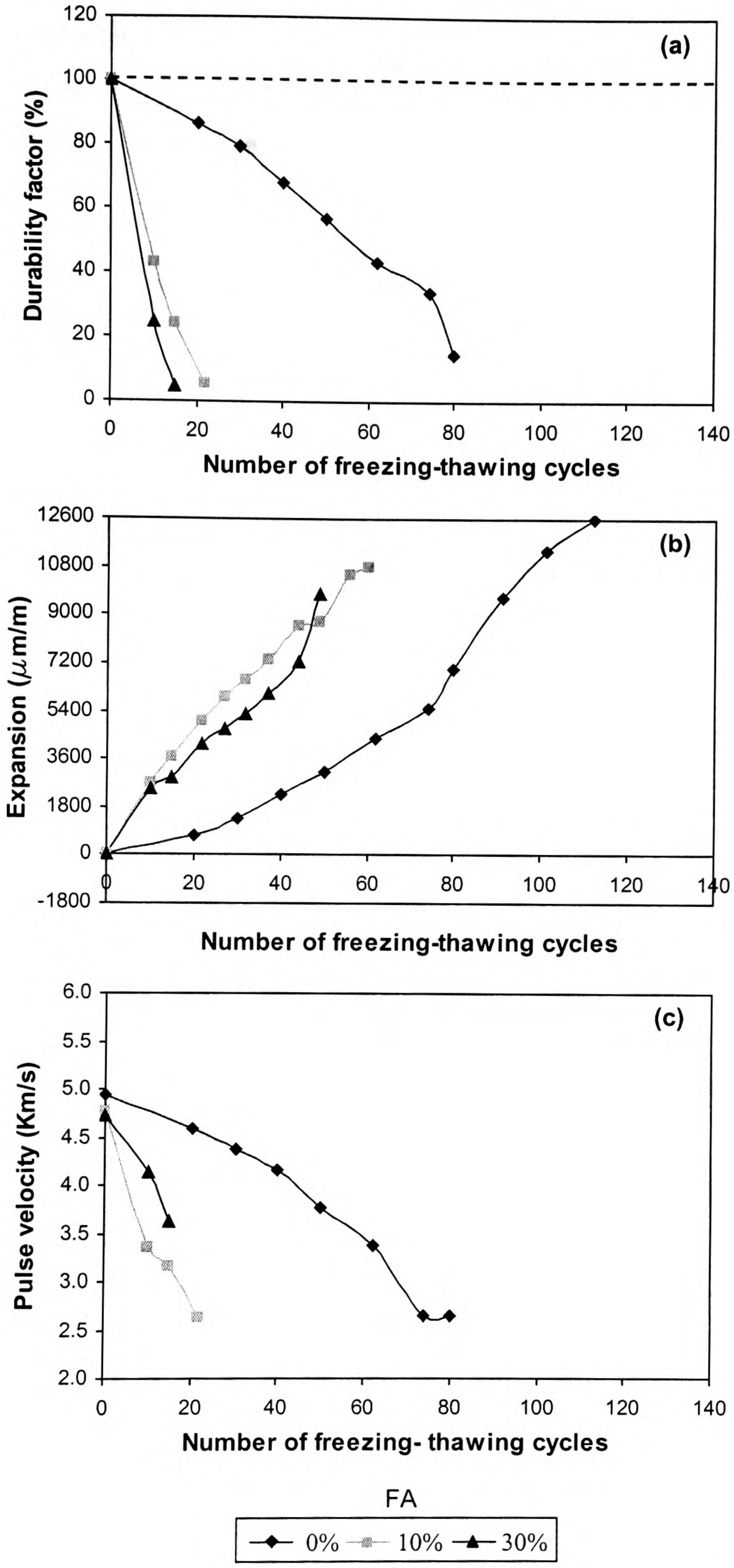


Figure 5.19 Influence of FA on (a) durability factor (b) expansion and (c) pulse velocity of non air-entrained FA concrete.

25% respectively after only 10 cycles of freezing and thawing. Similar deterioration was by the expansion and pulse velocity data shown in Figures 5.19(b) and (c). All three concretes soon suffered expansions well above 200 μm/m.

The test results characterizing the effects of FA on the DF, expansion and pulse velocity of air-entrained concrete are given in Tables B.9, B.15 and B.16 of Appendix B and presented graphically in Figures 5.20(a), (b) and (c). The results indicate that there was essentially no difference between FA and control concrete performances for the first 90 cycles of freezing and thawing. However beyond that point, as indicated by Figures 5.20(a) and (c), the 30% FA concrete slowly showed some decrease in DF and pulse velocity. All three concretes showed negligible expansions and if the criterion for failure based on a DF of less than 60% and an expansion bigger than 200 μm/m is followed then it can be concluded that all the air-entrained concrete performed satisfactorily after 120 cycles of freezing and thawing. This performance is consistent with that observed for the air-entrained MK concretes (see Figure 5.14).

Although the DF and pulse velocity measurements for the FA concretes were terminated at around 22 cycles, weight readings were continuously recorded until 67 and 49 cycles were reached for the 10% and 30% FA concretes, respectively. At that point the testing was terminated since the specimens were reduced to rubble. Figure 5.21 shows the weight changes with increasing number of freezing and thawing cycles. An important feature to note is that at the beginning of the test the FA concretes showed some increase in weight. This phenomenon is an indication of high water absorption due to a more porous matrix caused by the FA. The FA concretes suffered rapid weight loss after 20 cycles as indicated by the steep gradients of the 10 and 30% FA concretes. It is also important to note the consistency exhibited by the two specimens, i.e. BS 5075 and ASTM C666. A comparison between the weight losses of the corresponding air-entrained specimens is shown in Figure 5.22. As with the non air-entrained concrete, both specimens show that the 30% FA concrete suffers more weight loss than the control or 10% FA concretes. Figure 5.23 shows the condition of the ASTM C666 specimens after 120 cycles.

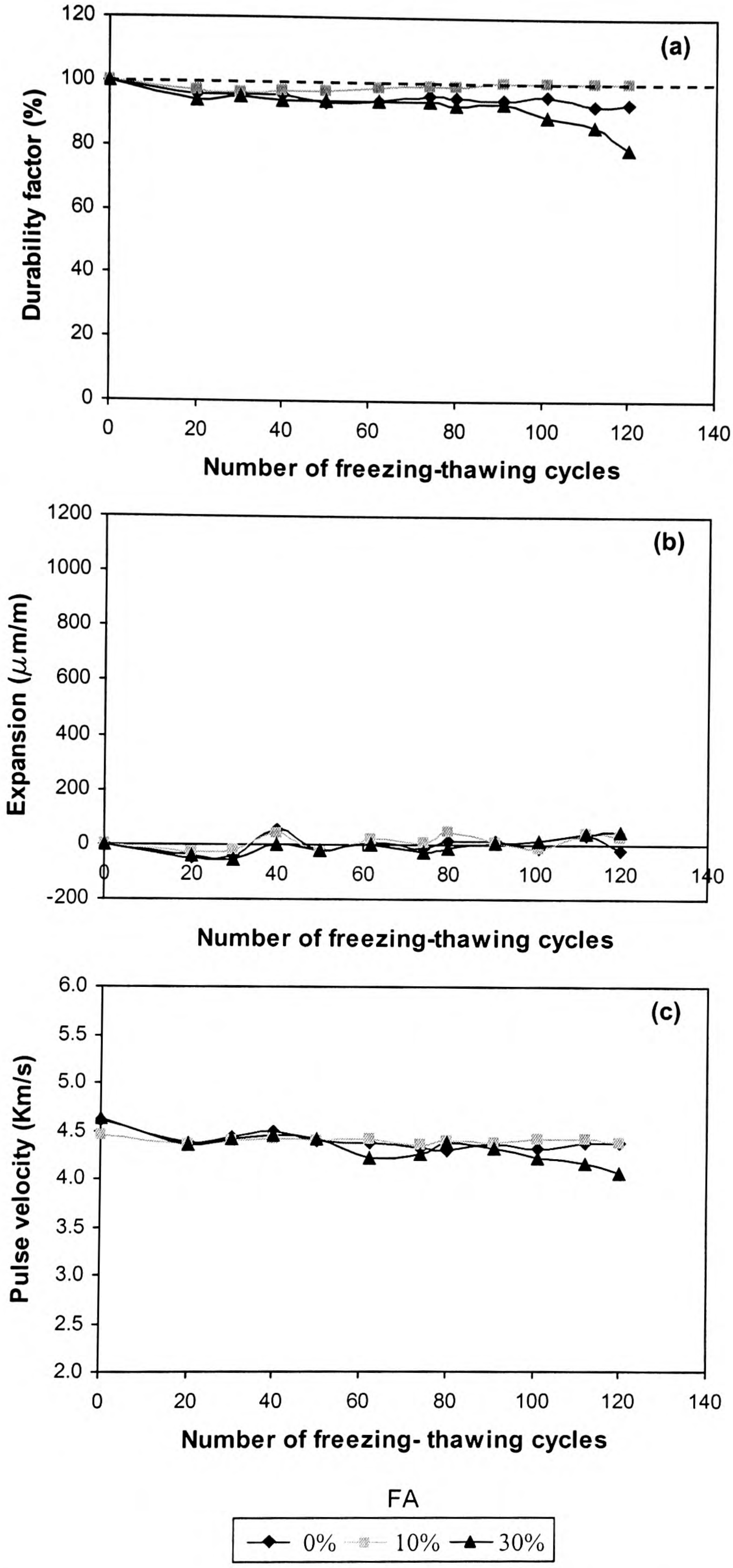


Figure 5.20 Influence of FA on (a) durability factor (b) expansion and (c) pulse velocity of air-entrained FA concrete.

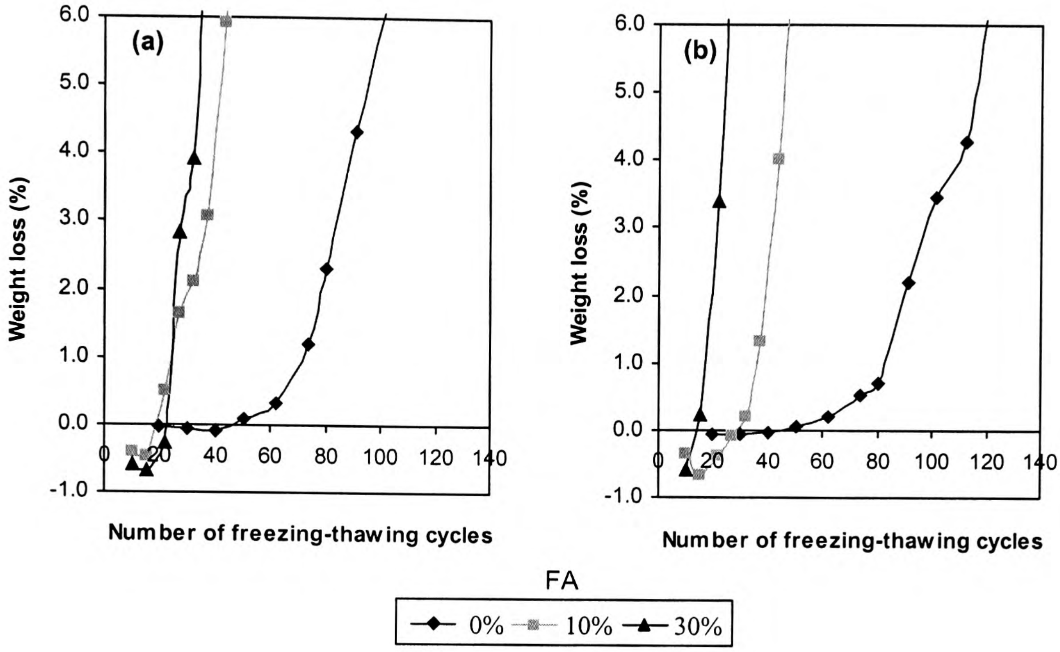


Figure 5.21 Influence of FA on weight loss of non air-entrained concrete for (a) BS 5075 specimen and (b) ASTM C666 specimen.

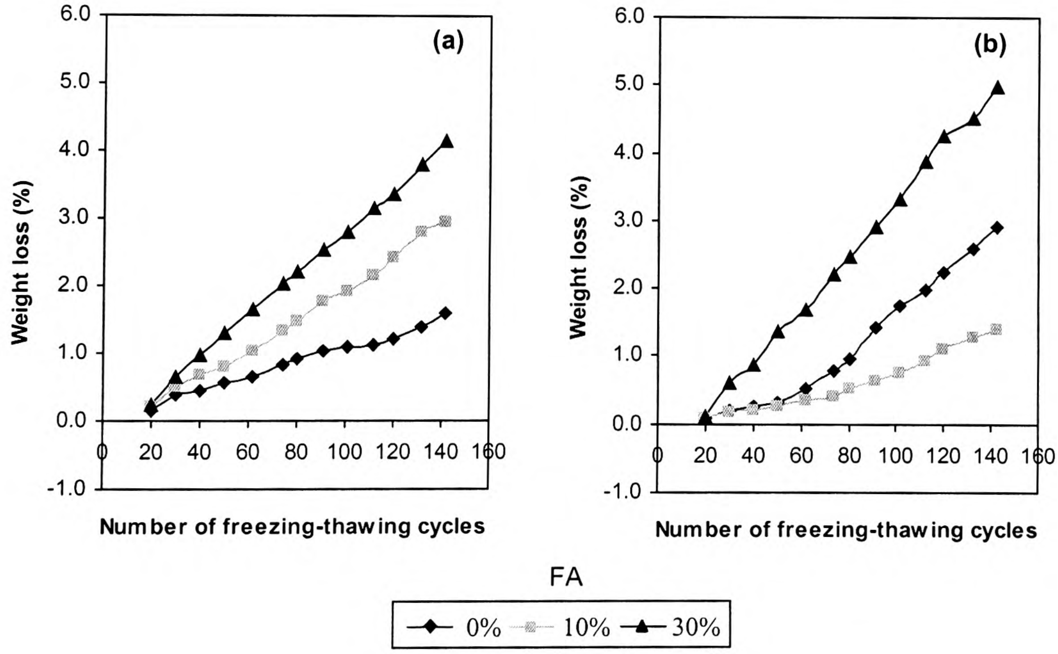


Figure 5.22 Influence of FA on weight loss of air-entrained concrete for (a) BS 5075 specimen and (b) ASTM C666 specimen.

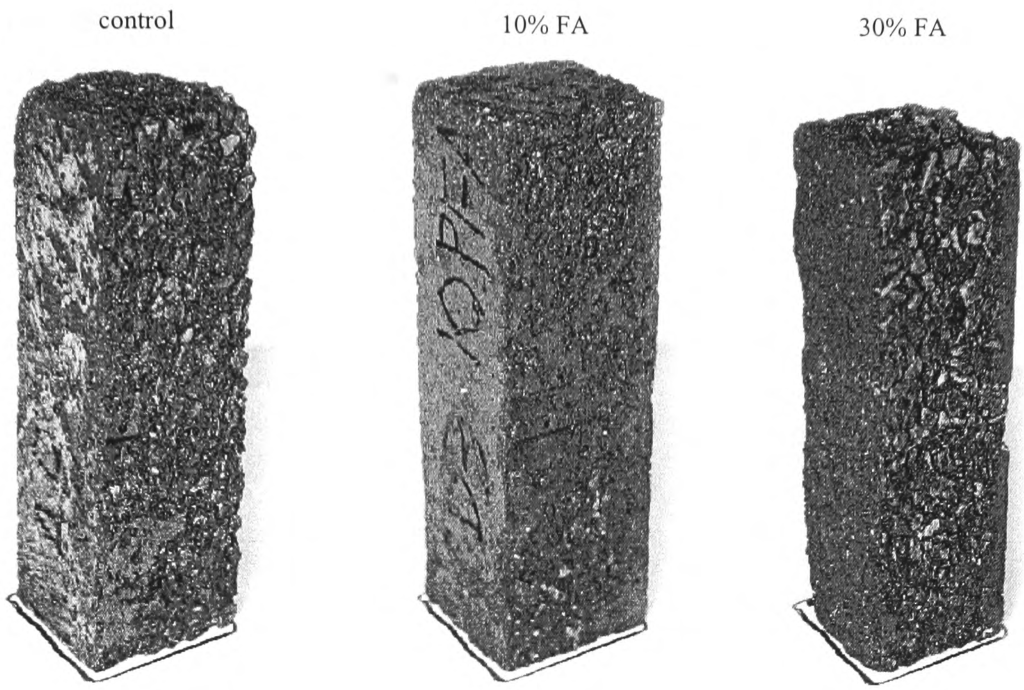


Figure 5.23 Condition of air-entrained control and FA concrete ASTM C666 series 2 specimens after 120 cycles of freezing and thawing.

The poor performance of FA concrete as compared to the control concrete (Figures 5.19 and 5.20) may be attributed to the slow reaction of the FA which results in insufficient strength of the paste to resist cracking caused by the action of frost and a much more permeable concrete. The results shown in Figures 5.10 give indication that the FA concretes continue to gain strength beyond 21 days, the point at which they were subjected to freezing and thawing, whereas the control concrete has developed maximum strength at 21 days. It must be emphasized, however, that although in general a relationship may exist between compressive strength and freeze-thaw performance, the latter, to much greater extent, is linked to the air void system and whether or not air is entrained.

Table 5.6 gives the compressive strengths for the non air-entrained and air-entrained concretes before and after freezing and thawing. It can be seen that the better performance exhibited by the air-entrained concrete over that of the non air-entrained concrete (Figures 5.19 and 5.20) was achieved despite the considerably lower compresssive strengths realised by the air-entrained concrete at the commencement of freezing and thawing testing. The condition of the non air-entrained specimens after 140 cycles was such that it was not possible to conduct any mechanical tests. It is worth mentioning that the inferior performance of the 30% FA concrete (Figure 5.20) may be related to the fact that this concrete gave the greatest (22%) weight loss.

Table 5.6 Compressive and flexural strengths of FA concrete after 120 cycles of freezing and thawing.

FA content (%)	*Compressive strength (N/mm^2)*		*Loss of strength (%)*	*Flexural strength At 120 cycles (N/mm^2)*
	At 21 days	*At 120 cycles*		
	Non air-entrained			
0	34.7	X	X	X
10	29.5	X	X	X
30	21.6	X	X	X
	Air-entrained			
0	24.7	20.3	18	4.4
10	19.8	16.5	17	4.5
30	17.2	13.5	22	2.5

Concrete at 10% total replacement level

This section presents the results of freeze-thaw performance of concretes containing MK, FA or blends of MK and FA at 10% total replacement for PC. Figures 5.24(a), (b) and (c) give the results for the DF, expansion and pulse velocity for the non air-entrained concretes. Based on all these measurements the MK concrete performed consistently better than all other concretes whereas the FA concrete showed consistently inferior performance. Although the ternary FA-MK blend shows improvement over the binary FA concrete, this still gave inferior performance compared to that of the control concrete. Based on the previously stated failure criterion (DF < 60%) the MK, control, FA-MK and FA concretes failed after 78, 50,

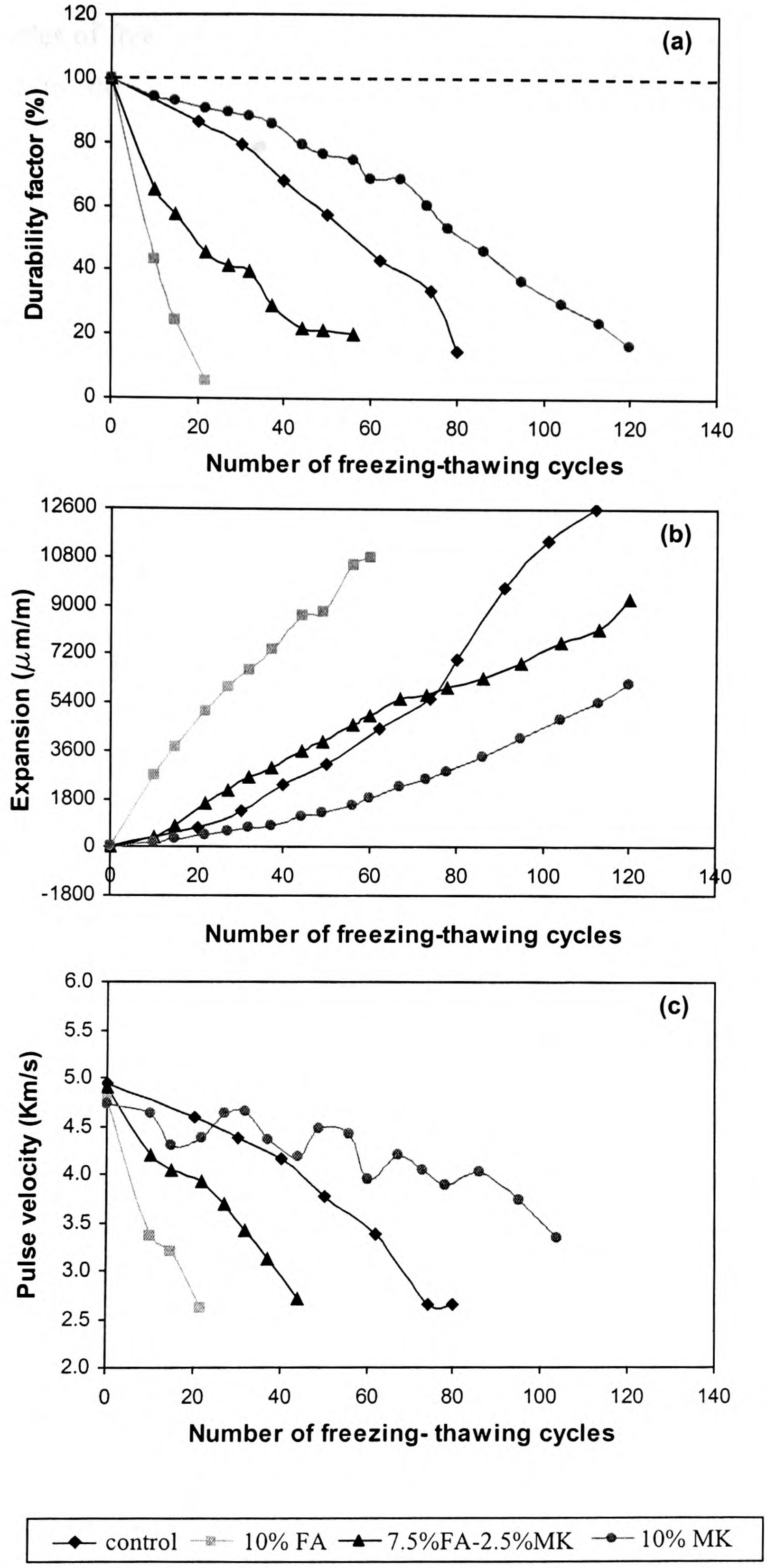


Figure 5.24 Influence of pozzolans at 10% total replacement level on (a) durability factor (b) expansion and (c) pulse velocity of non air-entrained.

20 and 10 cycles of freezing and thawing respectively. These premature failures can be attributed to the fact that no air was entrained in the concrete. Figure 5.25, which gives the results for the air-entrained concretes, shows that all concretes performed well up to 120 cycles of freezing and thawing. In general all the concretes irrespective of the pozzolanic material or blend of pozzolanic materials used were equally resistant to freeze-thaw action. This leads to the conclusion that the main controlling factor in maintaining good freeze-thaw durability is the air content of hardened concrete.

The results for the weight loss of the non air-entrained and air-entrained concretes at 10% total replacement level are shown in Figures 5.26 and 5.27, respectively. The concrete incorporating 10% FA, whether air-entrained or not, exhibited more scaling than the control, MK and FA-MK concretes. In all cases MK concrete gives the best performance particularly when air-entrainment is employed where little or no scaling takes place. These results are consistent with those shown in Figures 5.24 and 5.25. Usually for the non air-entrained concretes the weight loss included aggregate spalling at the very early stages of exposure to freezing and thawing. For this reason non air-entrained concretes showed rapid loss in weight as indicated by the steep gradients in Figure 5.26. Surface scaling in the air-entrained specimens took place at a much reduced rate.

Table 5.7 compares the results for the compressive and flexural strength of concretes with 10% total replacement. With the exception of the MK concrete the specimens without entrained air deteriorated to such an extent that they could not be tested for compressive and flexural strength. In the case of air-entrained concrete there was negligible change in compressive strength. The control and the FA concretes exhibited the greatest reduction in compressive strength.

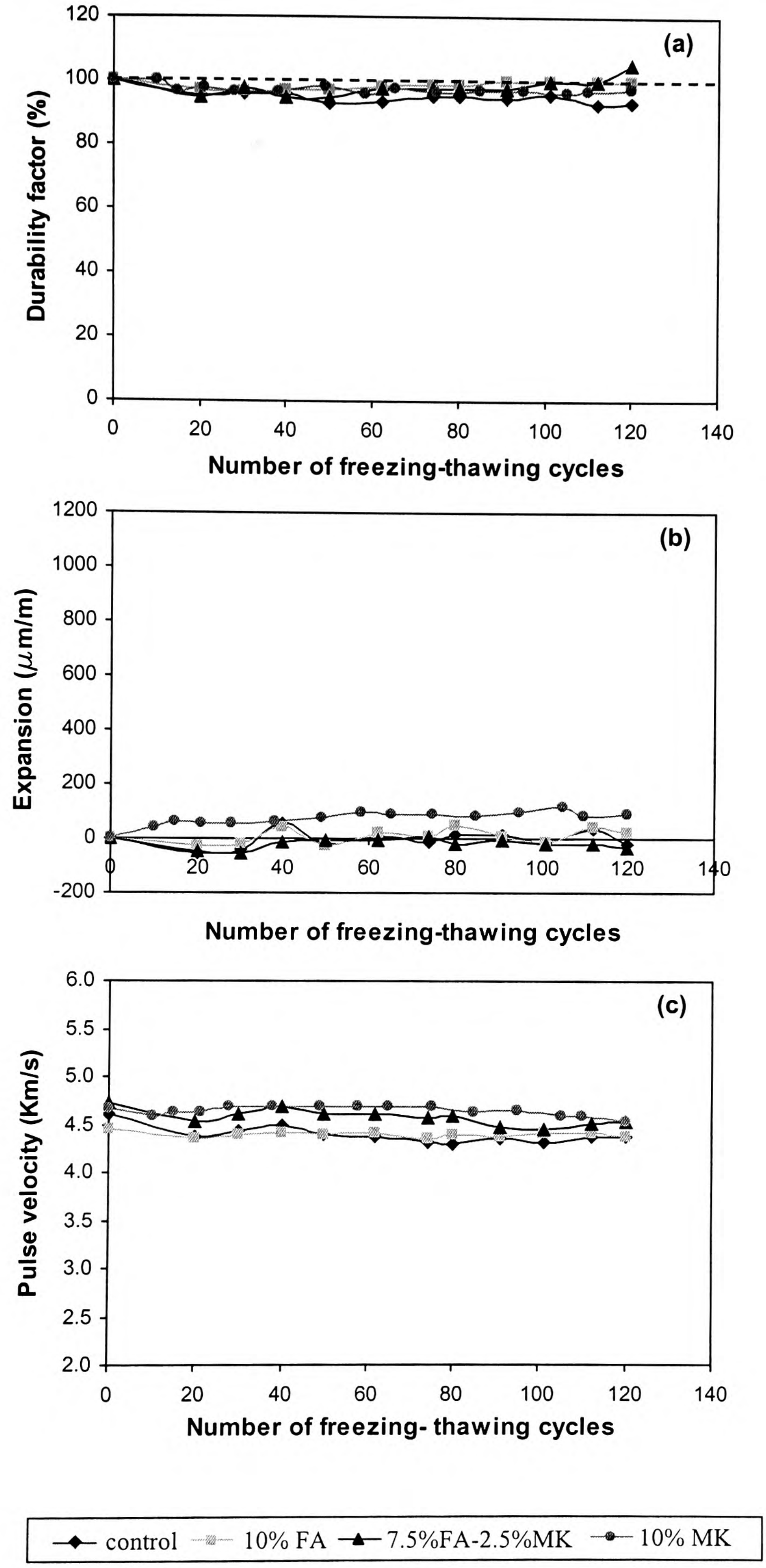


Figure 5.25 Influence of pozzolans at 10% total replacement level on (a) durability factor (b) expansion and (c) pulse velocity of air- entrained concrete.

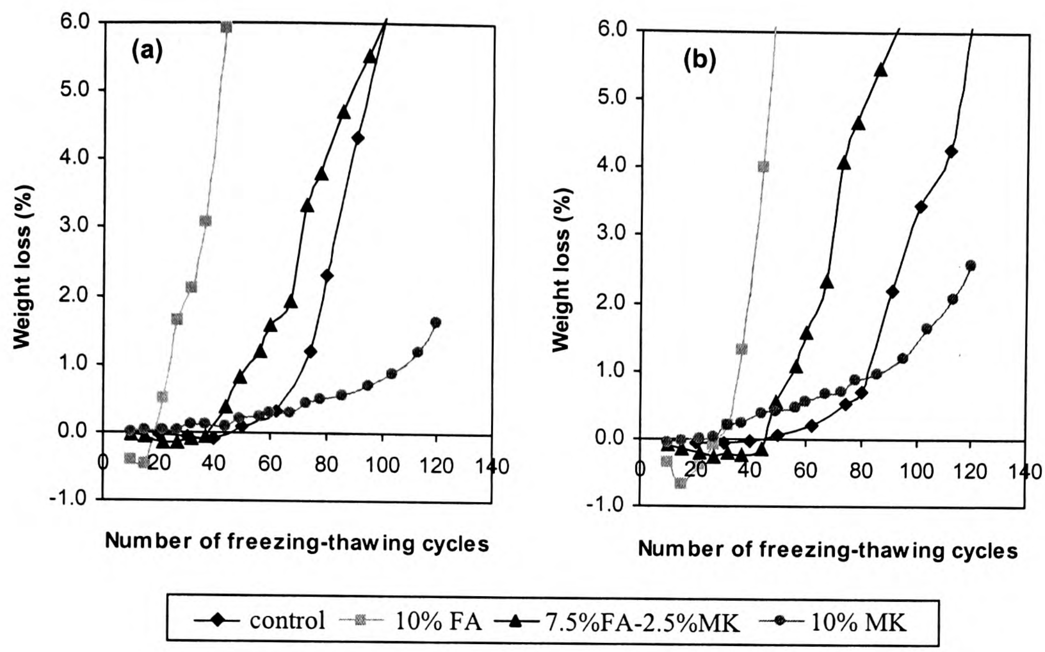


Figure 5.26 Influence of pozzolans at 10% total replacement level on weight loss of non air-entrained concrete, for (a) BS 5075 and (b) ASTM C666 specimens.

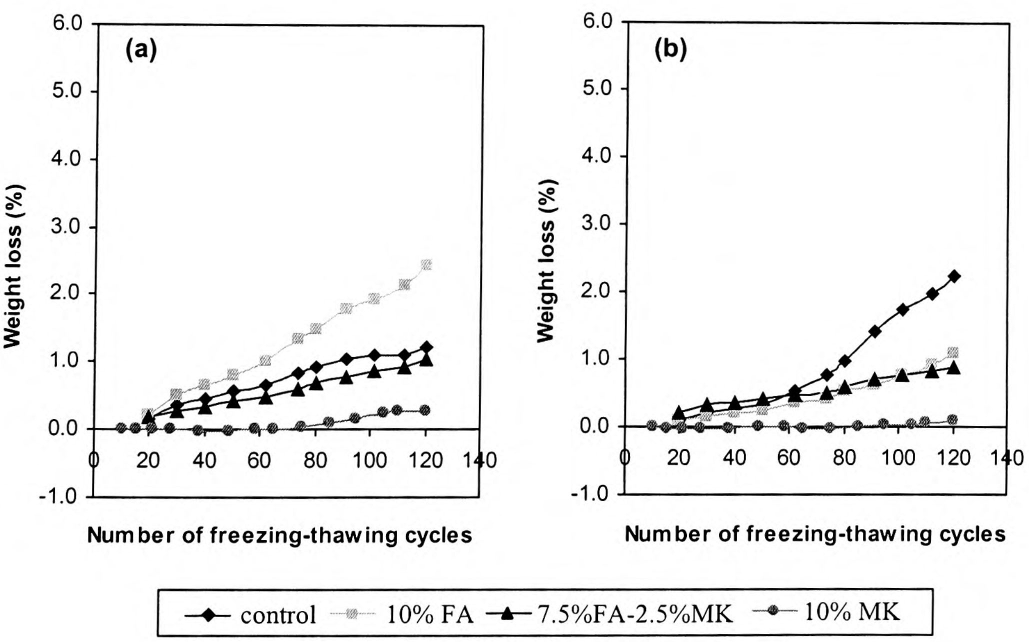


Figure 5.27 Influence of pozzolans at 10% total replacement level on weight loss of air-entrained concrete for (a) BS 5075 (b) ASTM C666 specimens.

Table 5.7 Compressive and flexural strengths of concrete at 10% total replacement level after 120 cycles of freezing and thawing.

Concrete	*Compressive strength (N/mm^2)*		*Loss of strength (%)*	*Flexural strength At 120 cycles (N/mm^2)*
	At 21 days	*At 120 cycles*		
	Non air-entrained			
control	34.7	X	X	X
10%FA	29.5	X	X	X
7.5%FA-2.5%MK	33.6	X	X	X
10%MK	45.0	21.2	53	1.2
	Air-entrained			
control	24.7	20.3	18	4.4
10%FA	19.8	16.5	17	4.5
7.5%FA-2.5%MK	26.9	26.3	2.2	5.8
10%MK	35.8	34.2	4	4.4

Concrete at 30% total replacement level

Figure 5.28 shows a comparison between the DFs, expansions and pulse velocities for non air-entrained concretes incorporating pozzolans at 30% total replacement. As in the case of 10% replacement (Figure 5.24), the replacement of PC by 30% FA results in deterioration in resistance to freezing and thawing as compared to that of the control concrete. It is interesting to note, however, that the significant improvement in performance obtained in the case of the ternary blend of FA-MK (FA:MK = 1:3) obtained at the 10% replacement level is not replicated in a significant way in the case of the 30% replacement. Although this may be due to the high level of replacement of PC by FA and the associated reduction in pozzolanic activity up to the age of 21 days, it will be shown later that, in fact, the reduction in strength at 21 days due to the incorporation of 30% FA is eliminated by further blending with MK. This is further evidence that the resistance to freezing and thawing action cannot directly be related to the compressive strength and that such resistance is more directly influenced by the air-void system of the concrete.

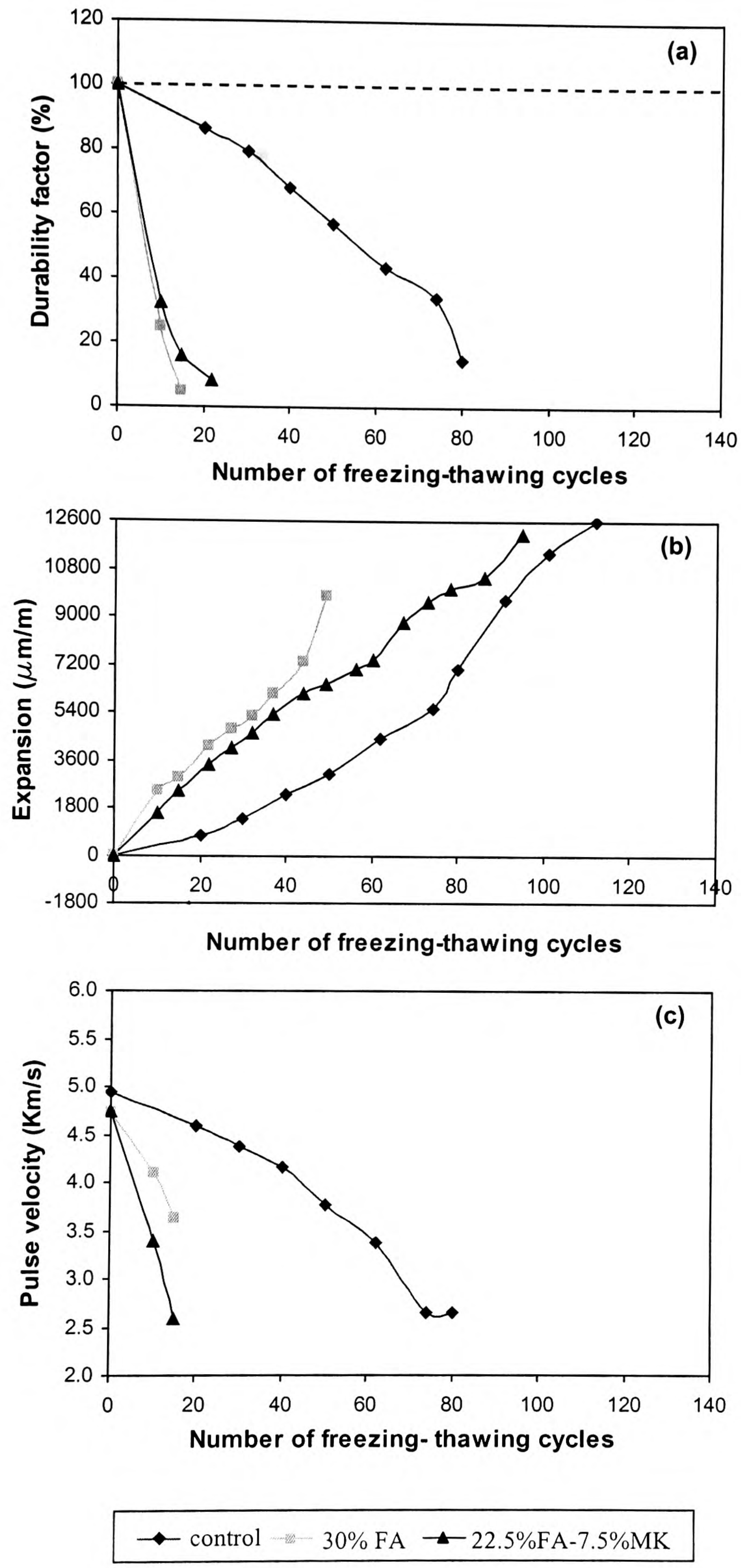


Figure 5.28 Influence of pozzolans at 30% total replacement level on (a) durability factor (b) expansion and (c) pulse velocity of non air-entrained concrete.

Figure 5.29 gives the results for the air-entrained specimens where it is immediately seen that all concretes, as in the case of 10% replacement, performed satisfactorily although at 30% replacement, blending FA with MK results in improved resistance as indicated by the results for DFs and pulse velocities.

The results for the weight loss are presented in Figures 5.30 and 5.31. Figure 5.30 shows that the use of pozzolans without air entrainment gives greater loss in weight than that exhibited by the control. Some improvement is obtained when the FA is blended with MK. The results in Figure 5.31 show that although air-entrained FA concrete appears to again give inferior performance to that of the control concrete, further blending with MK results in significant reductions in weight loss. The gain of weight at the initial stages of the freezing and thawing testing, a characteristic observed for all the non air-entrained concretes incorporating FA, suggests an open structure and that the level of MK in the system is probably not sufficient to develop a more closed porosity with which MK is normally associated.

Table 5.8 Compressive and flexural strengths of concrete at 30% total replacement level after 120 cycles of freezing and thawing.

Concrete	*Compressive strength (N/mm^2)*		*Loss of strength %*	*Flexural strength At 120 cycles (N/mm^2)*
	At 21 days	*At 120 cycles*		
	Non air-entrained			
control	34.7	X	X	X
30%FA	21.6	X	X	X
22.5%FA-7.5%MK	34.6	X	X	X
	Air-entrained			
control	24.7	20.3	18	4.4
30%FA	17.2	13.5	22	2.5
22.5%FA-7.5%MK	27.0	19.6	27	4.0

The results of the compressive and flexural strength at the end of freezing and thawing testing for the concretes at 30% total replacement level are presented in Table 5.8. Again it was not possible to conduct the mechanical tests on the non air-

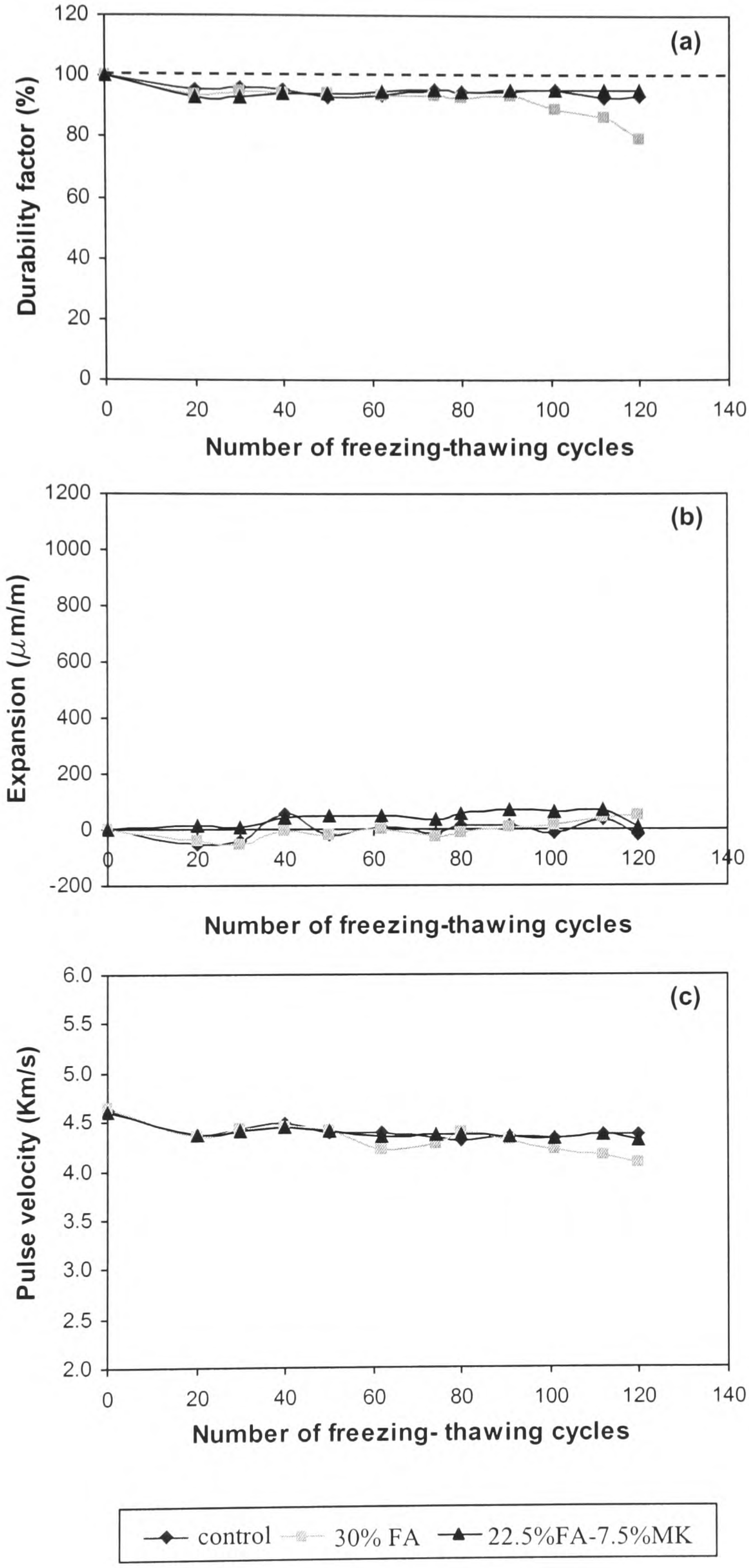


Figure 5.29 Influence of pozzolans at 30% total replacement level on (a) durability factor (b) expansion and (c) pulse velocity of air- entrained concrete.

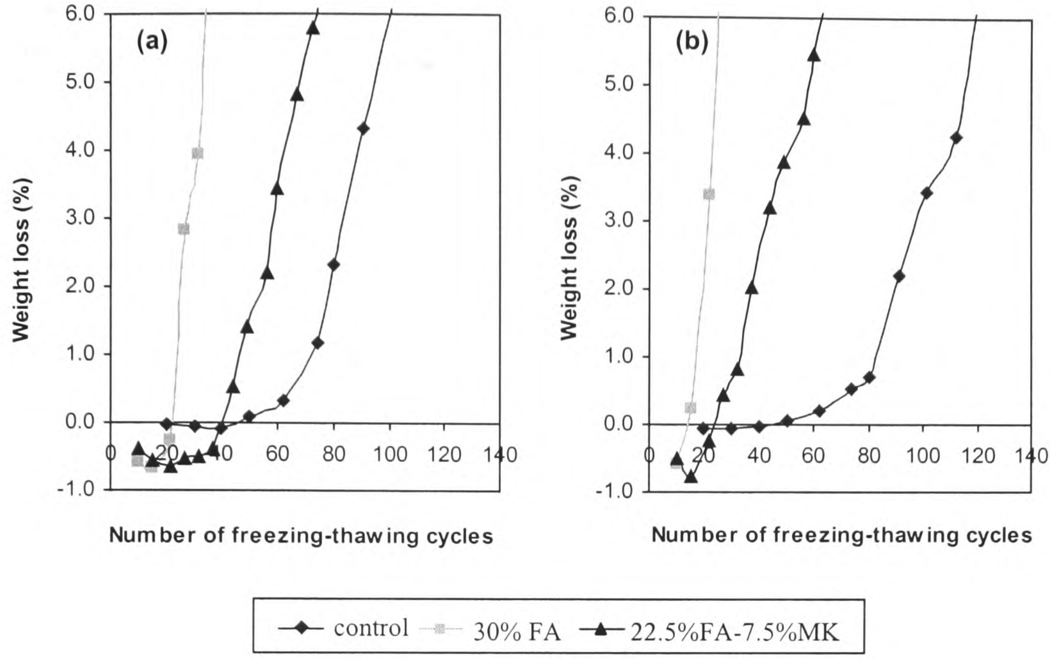


Figure 5.30 Influence of pozzolans at 30% total replacement level on weight loss of non air-entrained concrete, for (a) BS 5075 and (b) ASTM C666 specimens.

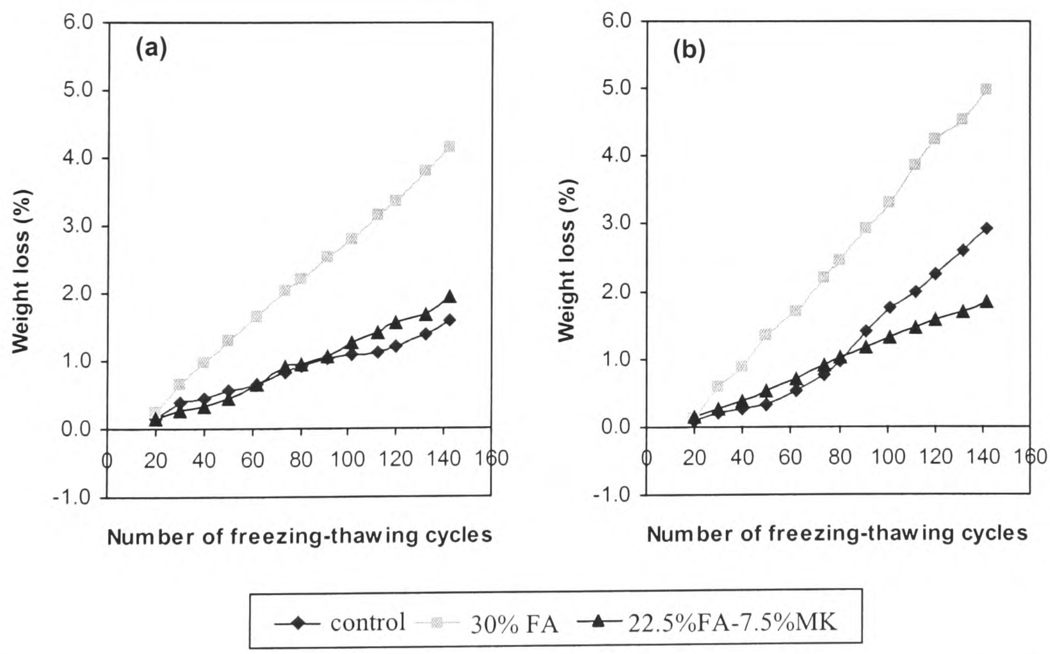


Figure 5.31 Influence of pozzolans at 30% total replacement level on weight loss of air-entrained concrete, for (a) BS 5075 and (b) ASTM C666 specimens.

entrained specimens because of the extent of deterioration developed. It is interesting to note that the reduction in compressive strength at 21 days caused by incorporating 30% FA in the specimens without air entrainment is overcome by further blending with MK. The lack of benefit in freeze-thaw resistance shown by the FA-MK concrete over that of the FA concrete, referred to earlier, is not linked to changes in compressive strength. Figure 5.32 shows the condition of the specimens with 30% total replacement at the end of freezing and thawing.

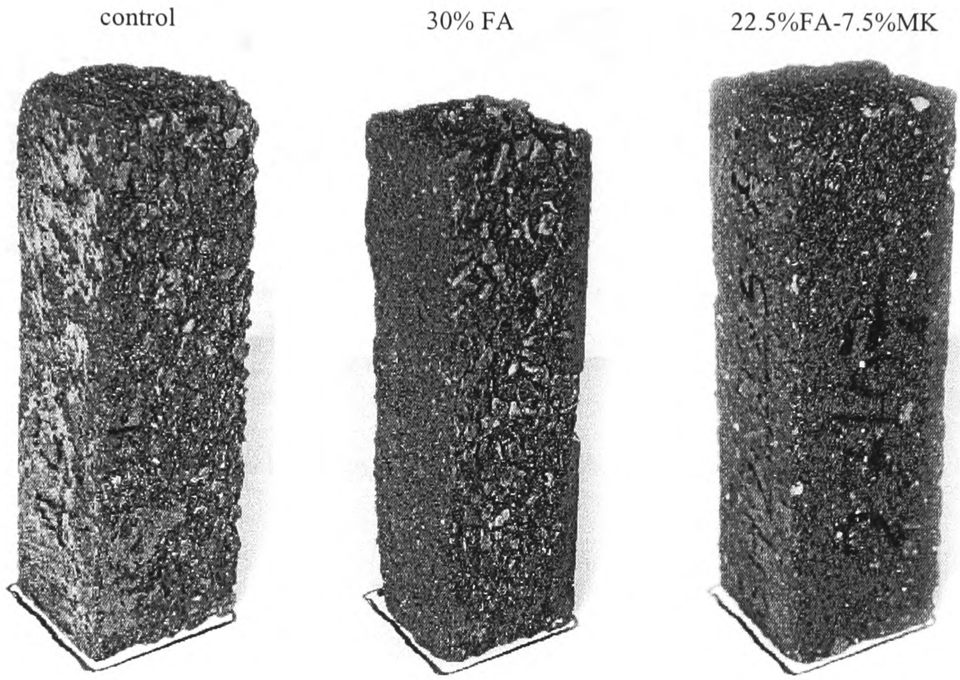


Figure 5.32 Condition of air-entrained control concrete specimen and concrete specimens incorporating pozzolans at 30% total replacement level, after 120 cycles of freezing and thawing.

5.4.3 Air-void system parameters

Section 3.4.4 of Chapter 3 gives an account of the optical microscopy technique used to determine the air-void parameters from polished sections of concrete cured for 21 days, the point at which freezing and thawing was applied. The definitions of all parameters investigated are given in section 5.2. Figure 5.33 gives the relationship between the air content of the hardened concrete and the fresh concrete. It is clear that a distinct correlation exists between the two sets of data and the high degree of correlation (R^2 = 0.90) is a good indicator of the validity and reliability of the procedures adopted in the study.

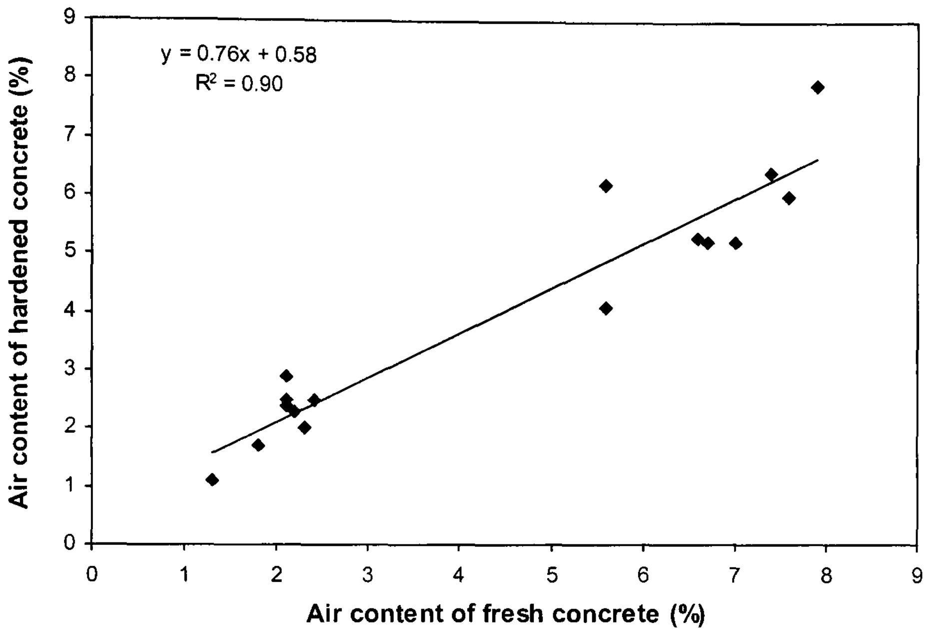


Figure 5.33 Relationship between air contents of fresh and hardened concretes.

As previously discussed all concretes will have accidentally entrapped air of the order of about 2% in the fresh state. The non air-entrained control concrete (see Figure 5.34(a)) has a spacing factor value of about 400 μm. The introduction of MK into the system appears to increase the spacing factor to a value of around 600 μm. This significant increase is attributed to the fineness of the MK particles, compared to PC particles, reflected by its high specific surface (14130 m^2/kg). The small MK particles act as fillers occupying some of the voids present in the paste, thus reducing their number and resulting in greater spacing factors. The present results do not show significant variation in the spacing factor caused by the level of MK in the system. This observation is supported by the results for the specific surface (Figure 5.34(b)) which show significant reductions in the cases of concretes incorporating MK. These reductions, again, appear to be constant and unaffected by the MK content. These remarks are further confirmed by the results for the number of voids per mm of traverse line (Figure 5.34(d)) which show marked reductions over the values of the control concrete as the MK content increases.

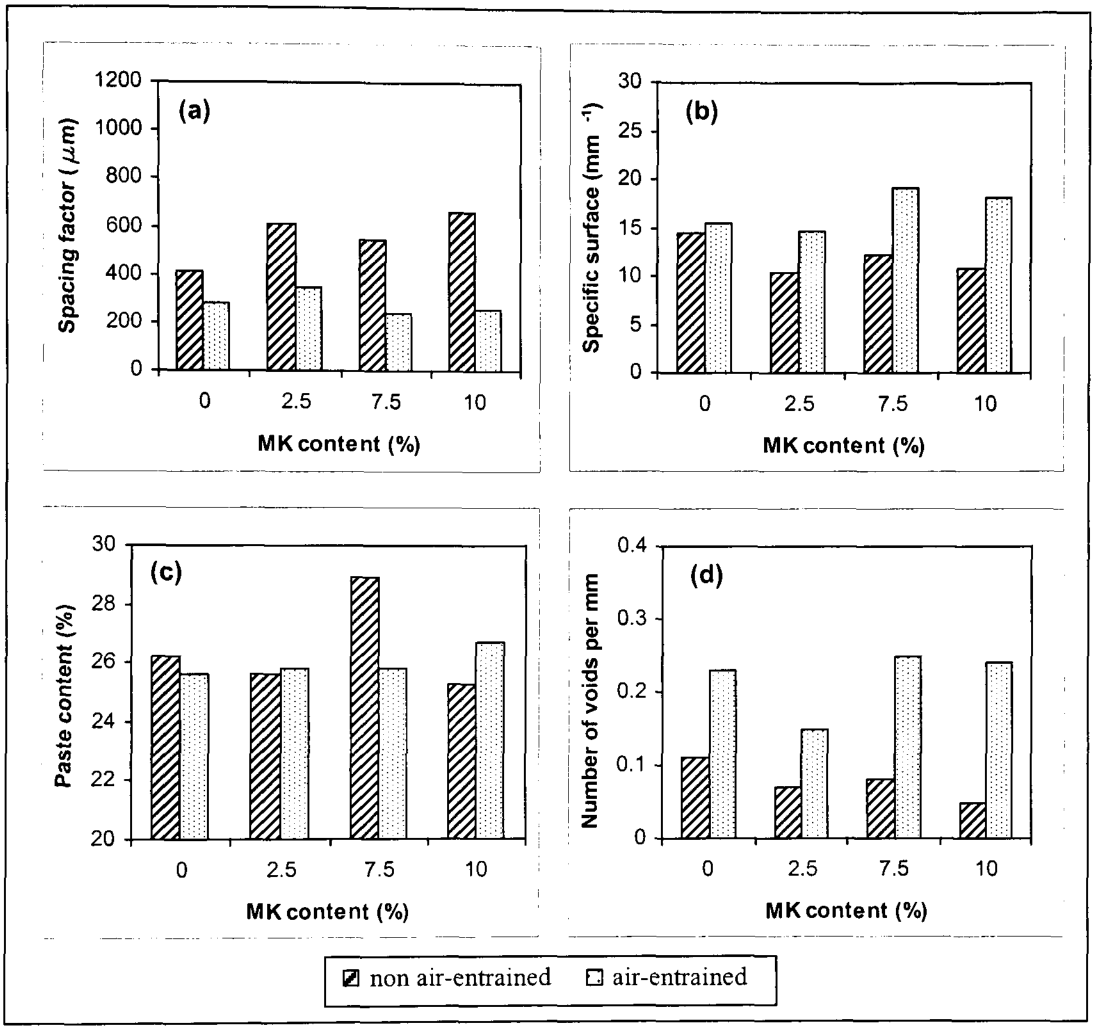


Figure 5.34 Influence of MK on (a) spacing factor, (b) specific surface, (c) paste content and (d) void frequency for non air-entrained and air- entrained concretes.

Figure 5.34(a) shows a marked reduction in the spacing factor of the control concrete as result of air-entrainment. Although the spacing factor in the air-entrained concrete increases when 2.5% MK is incorporated in the mixture, increasing amounts of MK appear to lead to reductions in the values of spacing factor. It is to be pointed out that the observed reductions are significant as we already have small values and further reductions are not normally easily achieved. This reduction in spacing factors correlate well with the measured values of the specific surface (Figure 5.34(b)), which show an increasing trend as the MK content increases.

The above gives an indication that the MK particles interact with the air entraining agent in a positive way in effecting greater dispersal of the entrained air resulting in lower spacing factors, higher specific surfaces and greater void frequencies. This explains the general improvements in the measured freeze-thaw parameters shown in Figures 5.24 and 5.25.

It would have been expected, in view of the relative densities of PC and MK that the incorporation of MK would result in an increase in paste content. Although some increases (Figure 5.34(c)) are observed at the higher MK contents, generally the increased paste content did not reveal consistent results with respect to increases in MK content. On the other hand, it may be argued that the paste content is not affected by the MK content whether or not air entrainment is employed. The main factor controlling the paste content was the water/binder ratio which was kept constant at 0.65.

Figure 5.35 gives the air-void parameters for the FA concretes. In general the influence of FA on the measured parameters i.e. spacing factor, specific surface and void frequency, is similar to that caused by MK. This, again, is attributed to the fineness and density of the FA particles relative to that of PC. In the case of the air-entrained concrete, the role played by FA in affecting the measured parameters is not consistent. It is to be emphasized that the incorporation of FA necessitated the addition of greater volumes of air-entraining agent (Chapter 4) in order to achieve the required air content (6%). Despite the achievement of the required air content, it appears that the interaction between the FA particles and the air-entraining agent is erratic and does not lead to systematic changes in air-void parameters with respect to increasing FA content. However, in general, as seen for MK concrete, the air-entrained FA concretes give better air void parameters than those of the non air-entrained concretes. This explains the great improvement in the freeze-thaw performance shown in Figure 5.29. Again the results for the measured paste content (Figure 5.35(c)) did not reveal consistent relationships with FA content.

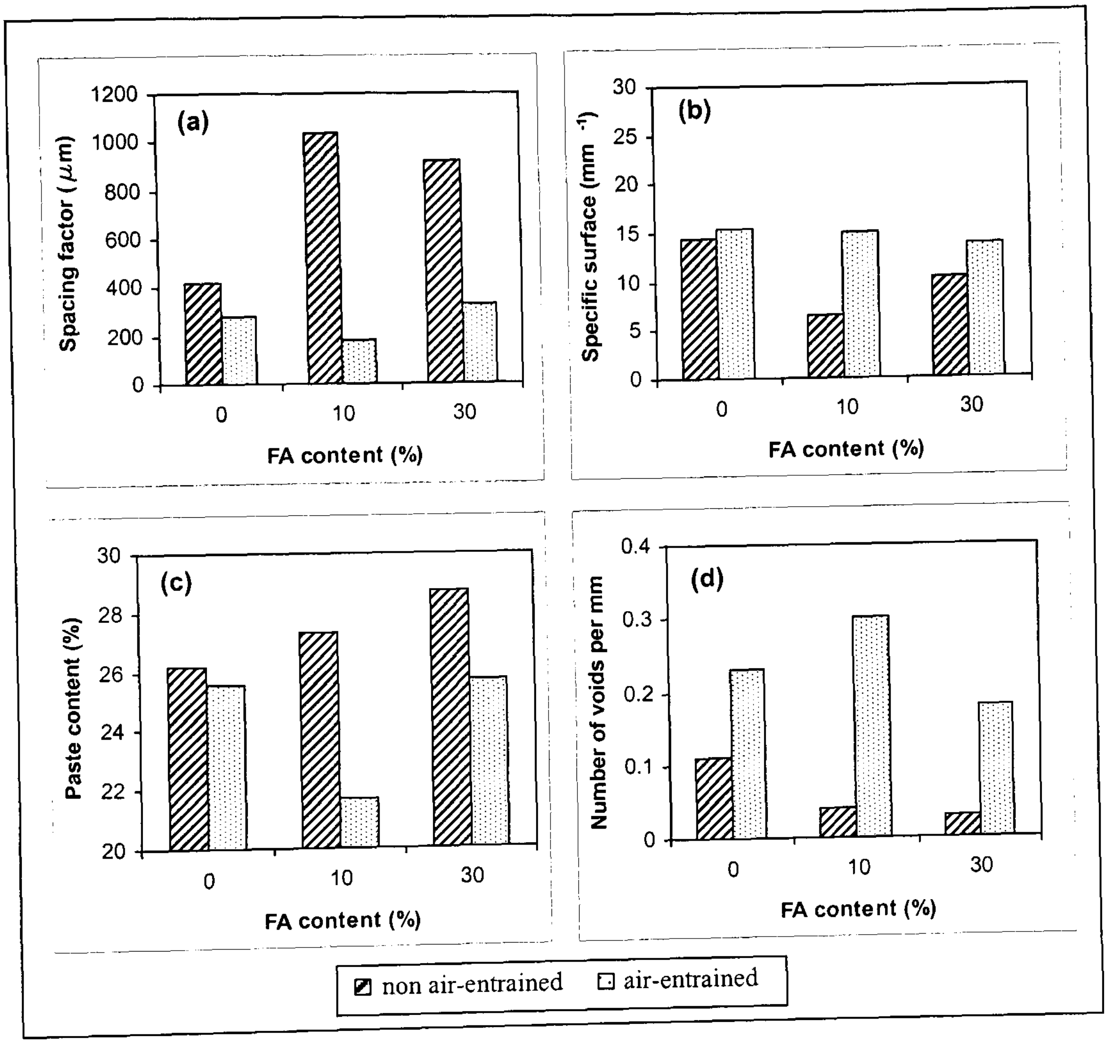


Figure 5.35 Influence of FA on (a) spacing factor, (b) specific surface, (c) paste content and (d) void frequency for non air-entrained and air- entrained concretes.

Figure 5.36 compares the measured parameters for the control and FA-MK ternary blended concretes at 10 and 30% total PC replacement. It is seen that the optimum values of spacing factor (< 200 μm), specific surface and void frequency are exhibited by the air-entrained ternary blend of FA-MK at the total replacement of 10%. These values confirm the good performance indicated by the freeze-thaw measurements shown in Figure 5.25 where almost zero expansion and negligible change in DF and pulse velocity were produced for this concrete.

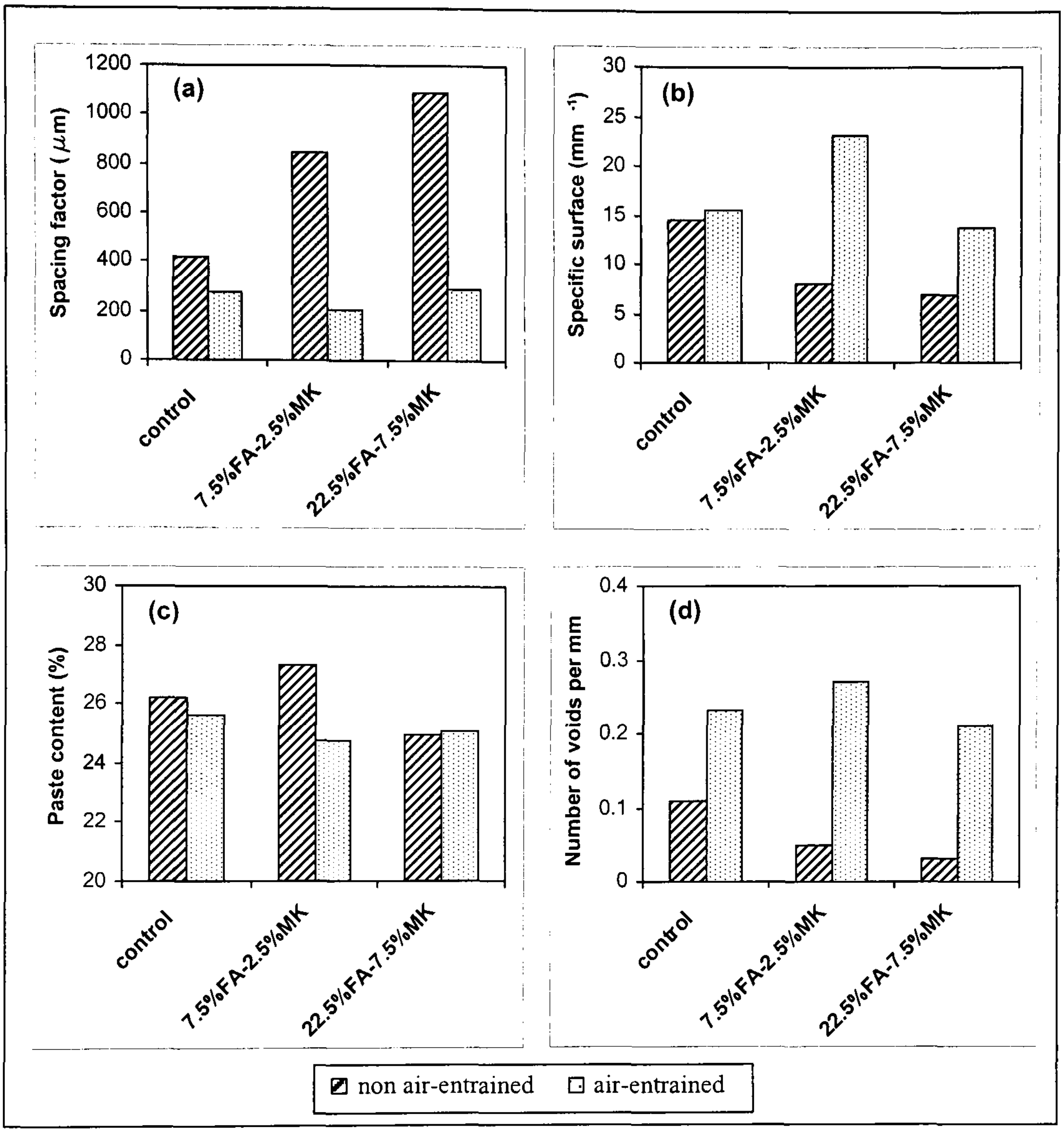


Figure 5.36 Influence of FA-MK blends on (a) spacing factor, (b) specific surface, (c) paste content and (d) void frequency for non air-entrained and air-entrained concretes.

5.5 Concluding remarks

Table 5.9 gives a summary of the freeze-thaw performance of concretes investigated in series 1 based on a criterion that unsatisfactory resistance to freezing and thawing corresponds to a DF less than 60% or a change in length greater than 200 μm/m. It is seen that although all concretes had DFs greater than 80% after 120 cycles of freezing and thawing, the control and 10% SF concretes failed at 79 and 124 cycles respectively with changes in length exceeding the 200 μm/m.

Table 5.9 Summary of the freeze-thaw performance of air-entrained concretes studied in series 1.

Concrete	*DF (%)*	*Change in length (μm/m)*	*No. of freezing-thawing cycles*	*Performance*
Control	78	224	79	Unsatisfactory
10% SF	96	276	124	Unsatisfactory
10% MK	97	112	124	Satisfactory
7.5% FA-2.5% MK	105	76	124	Satisfactory

Based on the same criterion, Tables 5.10 and 5.11 respectively give a summary of the freeze-thaw performance of the non air-entrained and air-entrained concretes examined in series 2. It is seen that the non air-entrained concretes performed poorly under freezing and thawing. However there is an indication that concrete containing 2.5 or 7.5% MK show enhanced resistance to freezing and thawing. The two concretes failed the change in length criterion at significantly greater number of freezing and thawing cycles compared to all other concretes. On the other hand, it is obvious that all the air-entrained concretes exhibited excellent performance under freeze-thaw conditions (DF > 60% and changes in length < 100 μm/m) irrespective of MK or FA content. However, there is an indication that the concrete incorporating 30% FA is the least resistant giving the lowest DF (79%). In general, the above observations underline the importance of air entrainment to ensure good freeze-thaw performance and at the same time indicate that MK up to 7.5% replacement level could be beneficial as far as frost resistance is concerned even in the absence of air entrainment.

Figure 5.37 presents the DFs versus expansion for all concretes investigated. It is clear that there is a linear relationship between the durability factor and expansion ($R^2 > 0.84$) irrespective of the concrete investigated. Due to the absence of entrained

Table 5.10 Summary of the freeze-thaw performance of non air-entrained concretes studied in series 2.

Concrete	*DF (%)*	*Change in length ($\mu m/m$)*	*No. of freezing-thawing cycles*	*Performance*
Control	86	709	20	Unsatisfactory
2.5% MK	93	219	85	Unsatisfactory
7.5% MK	93	247	75	Unsatisfactory
10% MK	93	291	15	Unsatisfactory
10% FA	43	2681	10	Unsatisfactory
30% FA	25	2458	10	Unsatisfactory
7.5%FA-2.5%MK	65	398	10	Unsatisfactory
22.5%FA-7.5%MK	33	1618	10	Unsatisfactory

Table 5.11 Summary of the freeze-thaw performance of air-entrained concretes studied in series 2.

Concrete	*DF (%)*	*Change in length ($\mu m/m$)*	*No. of freezing-thawing cycles*	*Performance*
Control	94	-24	120	Satisfactory
2.5% MK	99	56	120	Satisfactory
7.5% MK	98	8	120	Satisfactory
10% MK	98	88	120	Satisfactory
10% FA	100	24	120	Satisfactory
30% FA	79	-48	120	Satisfactory
7.5%FA-2.5%MK	105	-36	120	Satisfactory
22.5%FA-7.5%MK	96	8	120	Satisfactory

air when the concretes are subjected to freezing and thawing internal cracking starts to take place. This means that there is space for more ice to be formed during freezing and therefore expansion is caused. As the freezing and thawing progresses more ice is formed and consequently more expansion takes place. At the same time internal cracking causes a decrease in the transverse frequency which results in a decrease in the DF. Similarly Figure 5.37(b) presents the DF versus expansion for the

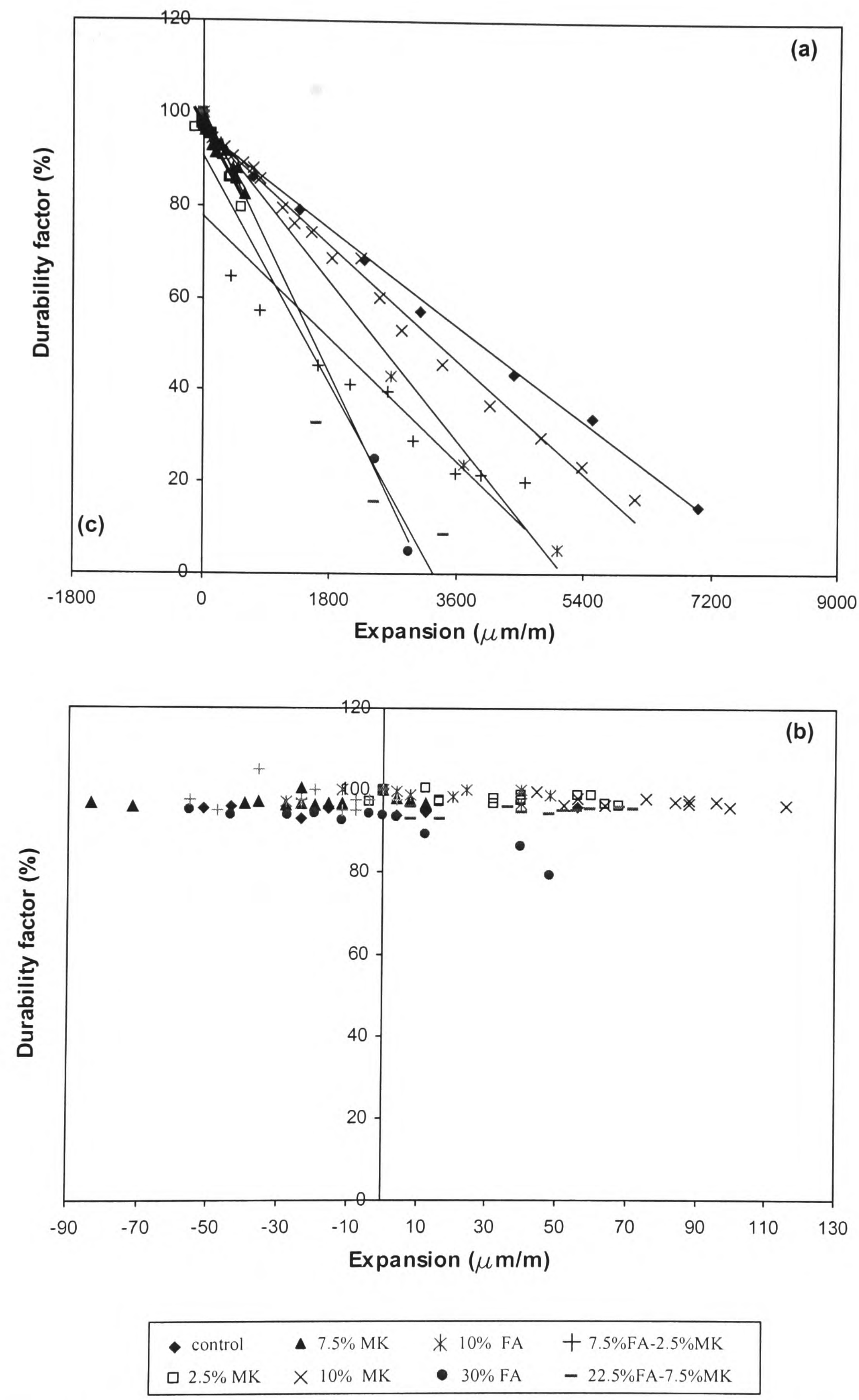


Figure 5.37 Relationship between durability factor and expansion for (a) non air-entrained and (b) air-entrained concretes.

air-entrained concretes. As might be expected no relationship revealed between the two quantities because the concretes were air-entrained. However, it is confirmed that excellent freeze-thaw performance corresponds to expansions of values less than 200 μm. In fact the expansions for the air-entrained concretes ranged between approximately –90 and 130 μm/m.

Figure 5.38(a), which shows expansion against weight loss (recorded for ASTM C666 specimens) for the non air-entrained concretes, clearly confirms that there is also a strong correlation between expansion and weight loss due to freeze-thaw action. Even the results for some of the air-entrained concretes shown in Figure 5.38(b) confirm a good relationship between expansion and weight loss, although in general this relationship is not revealed because the concretes are air-entrained. This may indicate that the basic mechanisms responsible for scaling are not very different from those causing internal cracking and thus expansion. Briefly it can be said that the tensile stresses due to the action of frost can easily cause cracking and loss of small paste particles at the surface of the concrete.

As indicated previously in the literature review (see chapter 2) a minimum value for the spacing factor of 200 μm is specified for durable concrete in frost conditions. However, as shown in Figure 5.39, spacing factors for virtually all the durable concretes (DF > 60 %) are in the range between 200 and 400 μm. The results also indicate that the freeze-thaw performance declines at spacing factors above 400 μm, except in the cases of non air-entrained concretes incorporating 2.5 and 7.5% MK. These two concretes survived the 120 cycles of freezing and thawing with high durability factors, although their spacing factors were close to 600 μm. Thus, it is suggested that, depending on the pozzolanic composition of the blend (if used), higher values of spacing factor can be tolerated with respect to obtaining good freeze-thaw resistance. Furthermore, it would appear that the air-entrained concrete with high percentages of FA, in this case 30%, are less durable than the other air-entrained concretes, possibly suggesting that reduced spacing factors are required at this replacement level to ensure enhanced freeze-thaw durability. However, given the limited data, the above observations warrant further testing for confirmation.

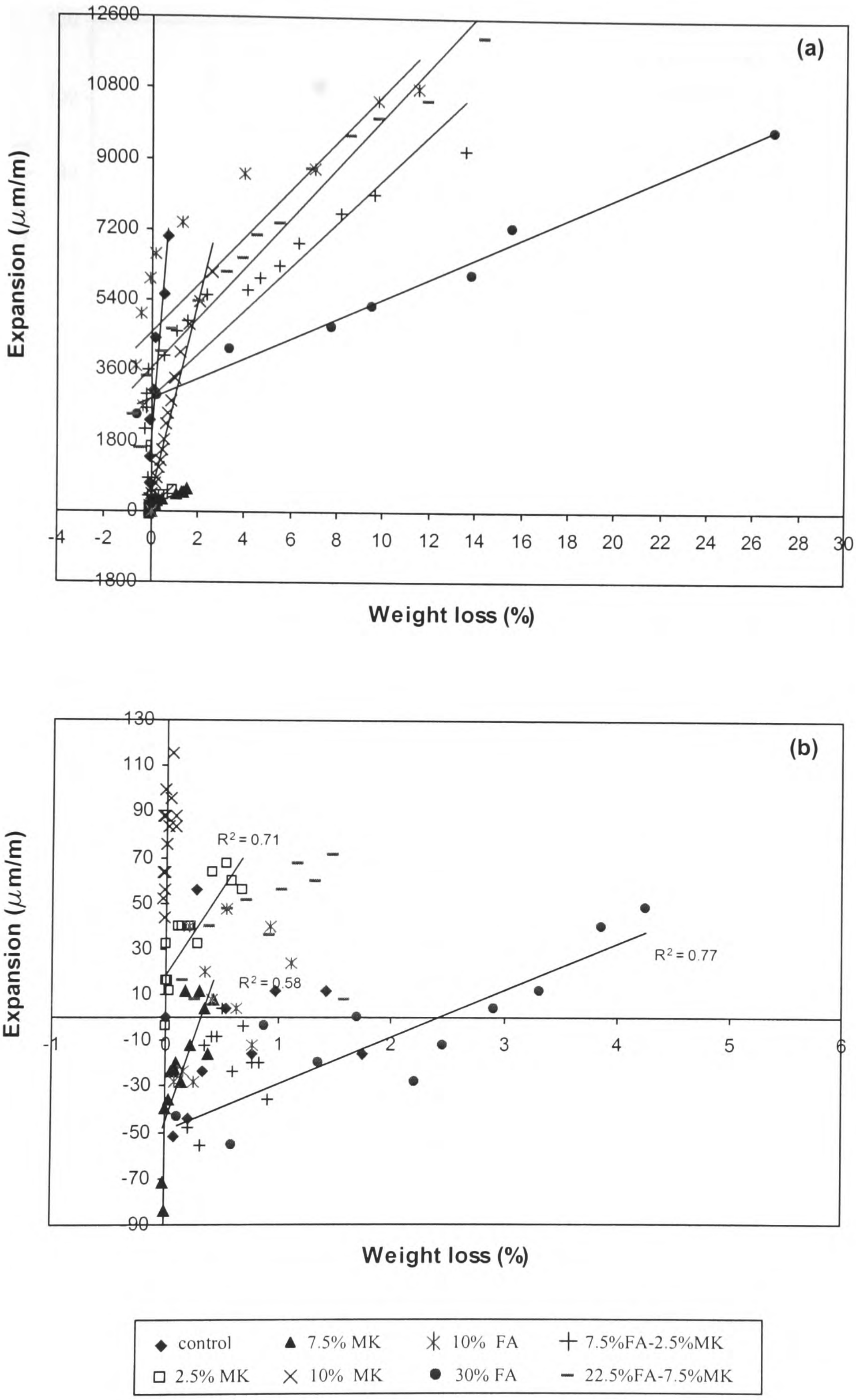


Figure 5.38 Relationship between expansion and weight loss for (a) non air-entrained and (b) air-entrained concretes.

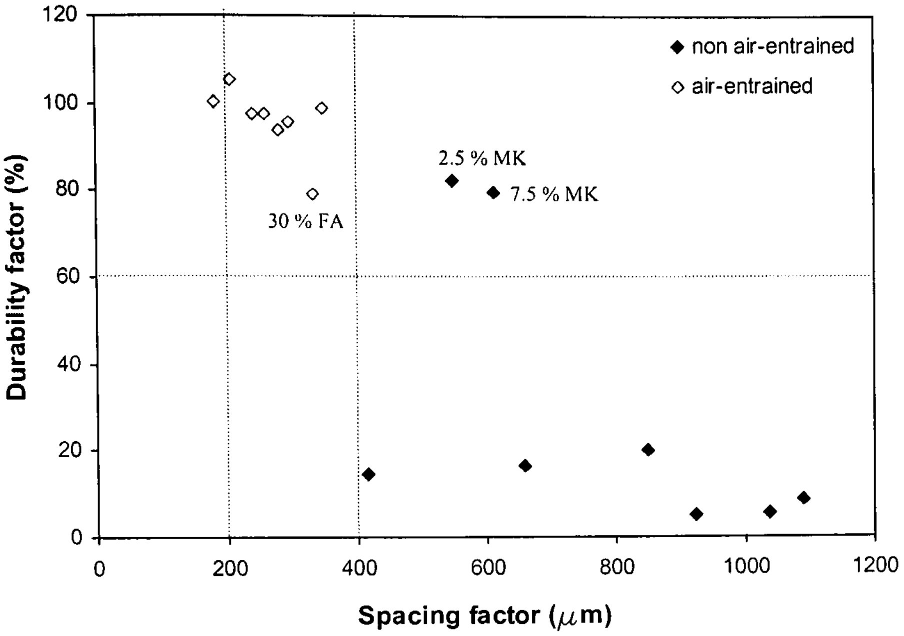


Figure 5.39 Relationship between durability factor at end of testing and spacing factor for all concretes.

Chapter 6 – Porosity and water absorption

This Chapter investigates the influence of MK, FA or blends of the two pozzolans on porosity, pore size distribution, sorptivity and water absorption and attempts to establish relationships between these parameters and the freeze-thaw data presented in Chapter 5. The Chapter is introduced with some details on how MIP data are interpreted and presents results of the porosity and pore size distribution of concretes as determined by MIP. It also describes the way sorptivity and water absorption are determined and continues with the presentation of the sorptivity and water absorption results. Full details as to the methodology of the investigations undertaken can be found in section 3.4.6. The results presented in this Chapter are grouped and presented in the same manner as that employed in presenting the freeze-thaw results in Chapter 5.

6.1 Porosity and pore size distribution

6.1.1 Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry (MIP) is the common method used to determine the porosity and pore size distribution of cement based materials. The method has been successfully used in many studies on hydrated cement pastes and mortars e.g. Cook and Hover [1999] and O'Farrell et al. [2001a]. Cook and Hover [1993] extended the applicability of the method to concrete. Unfortunately, the method suffers from a number of problems when applied to the complex pore structure in cementitious systems. The method of sample drying can influence pore size distributions [Zhang and Glasser, 2000] as can sample size [Hearn and Hooton, 1992] and selection of contact angle [Shi and Winslow, 1985].

MIP consists of enclosing a porous sample in a chamber, evacuating it and surrounding it with mercury. Monitored increments of pressure are then applied and the volume of mercury forced into the sample is measured. The resulting intruded volumes of mercury can be normalized in a variety of ways such as dividing the volume by sample weight, thus measured in units such as mm^3/g. The pressures that force the intrusion can be converted to equivalent pore sizes using a form of the Washburn equation [Cook and Hover, 1993]:

$$r = \frac{-2\gamma\cos\theta}{P} \qquad [6.1]$$

where r is the radius of the intruded pores, γ is the surface tension of mercury, θ is the angle of contact between mercury and the pore walls, and P is the pressure at which a given increment of mercury intrudes the pore system. The values of surface tension and contact angle of the mercury used in the present study are 0.48 N/m and 141.3°, respectively. It should also be noted here that the above model invokes the assumptions that the pores are (a) cylindrical and (b) entirely and equally accessible to the outer surface of the specimen [Diamond, 2000] which in practice is not the case. It therefore overestimates the volume of fine pores. However as a comparative method to assess the relative porosities of different cementitious materials it is still of great value.

An example of a cumulative pore volume versus equivalent pore size curve is provided in Figure 6.1. The plot represents one of the control mixtures used in this investigation. The greatest cumulative volume on this curve (corresponding to the highest pressure and the smallest equivalent pore size) is an estimate of the total porosity of the sample. The equivalent pore size corresponding to the steepest slope of the curve is that pore size through which mercury penetrates the bulk of the sample. This characteristic pore size is sometimes referred to as the threshold pore size and is defined as the pore size at which there is a sudden increase in the number, and therefore the cumulative volume, of pores that can be intruded by mercury. It is observed as a sudden marked increase in the rate of mercury intrusion into the

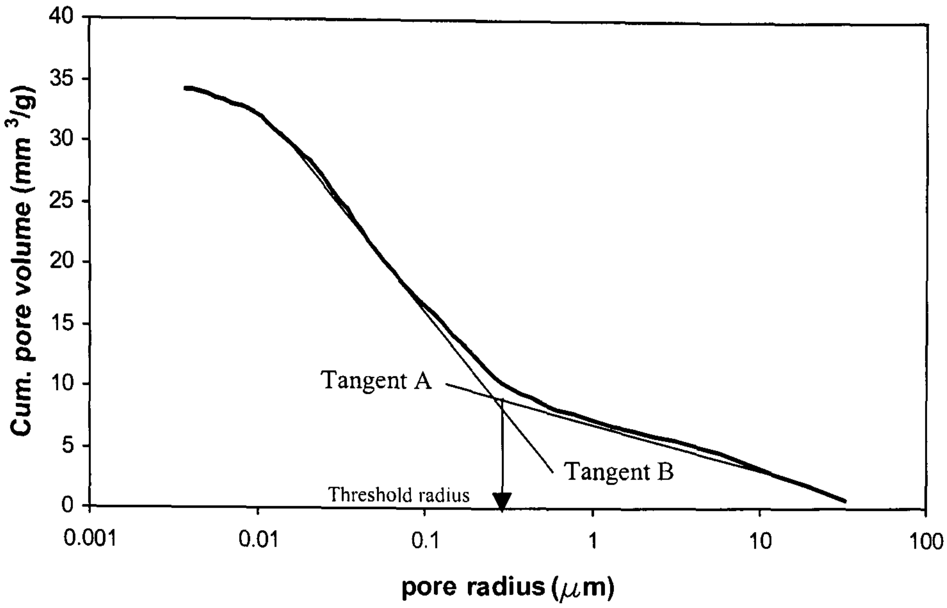


Figure 6.1 Typical MIP curve obtained for the air-entrained control concrete investigated in series 2.

sample and is estimated by drawing the tangents A and B as shown in Figure 6.1 and taking the intersection point as the threshold radius. In Figure 6.1 the cumulative volume curve indicates a total cumulative volume of 35 mm^3/g and a threshold radius of approximately 0.2 μm. The data obtained from the MIP test can also be used to estimate the percentage of total pore volume that is made up from pores of radii < 0.05 μm. The pore size of 0.05 μm is usually taken as a measure of pore refinement as this corresponds approximately with the lower end of the capillary pore size range and is easily obtainable utilizing MIP [Hearn and Young, 1999].

6.1.2 Results and discussion

From the MIP data gathered in this investigation which are presented below, it was found that the percentage of total pore volume that is made up from pores of radii < 0.05 μm, the threshold radius and the total porosity represent the most reliable parameters for characterizing the porosity of the concretes. The values reported were calculated by averaging the results obtained from four independent runs conducted on four different samples. In certain cases where the variability of the four results was high the three best values were used. While cumulative intruded pore volume (see Figure 6.1) can also be used as an indication of the pore refinement, it was not used in this investigation since the variability of the values between the four values was high. This was attributed to the possible presence of small aggregate particles in the samples of mortar, taken from the concrete. While the samples conventionally used for MIP studies can be either powder, granular pieces or specimens cast to the same dimension and shape as that of the sample cell itself, for concrete one may use pieces of mortar separated from the parent concrete [Hearn and Hooton, 1992] or a number of complete pieces of concrete inclusive of the coarse aggregates. The porosity obtained using a mortar chunk alone is likely to be higher than that of the parent concrete, as aggregates are relatively less porous. However, Laskar et al. [1997] recently demonstrated that a concrete chunk inclusive of coarse aggregates, instead of a chunk of extracted mortar is also a reliable form of material to be used in MIP studies for evaluation of pore structure of concrete, as long as the sample size is appropriate and the number of samples tested is kept high, usually above 4.

Metakaolin concrete

Figure 6.2 gives the MIP data for the non air-entrained and air-entrained control concrete and concretes with 2.5, 7.5 and 10% MK replacement of cement. The values can be seen in Tables D.1 to D.3 in Appendix D. The percentage of the total pore volume which is made up from pores of radii < 0.05 μm was taken as a measure of pore refinement. The results indicate that the air-entrained concretes have a lower proportion of pores with radii < 0.05 μm than the non air-entrained concretes, at all replacement levels. Also pore refinement increases with increasing amounts of the pozzolan for both the non air-entrained and air-entrained concretes. The value of threshold radius also reflects the pore refinement in the concretes. In line with the results of the total pore volume made up from pores of radii < 0.05 μm, the threshold radius is larger for air-entrained concretes as compared to those for non air-entrained concretes. Furthermore, the threshold radius decreases with increasing amounts of MK. Regarding total porosity, it is observed that irrespective of whether or not air entrainment is applied the porosity initially increases when 2.5% MK is used and

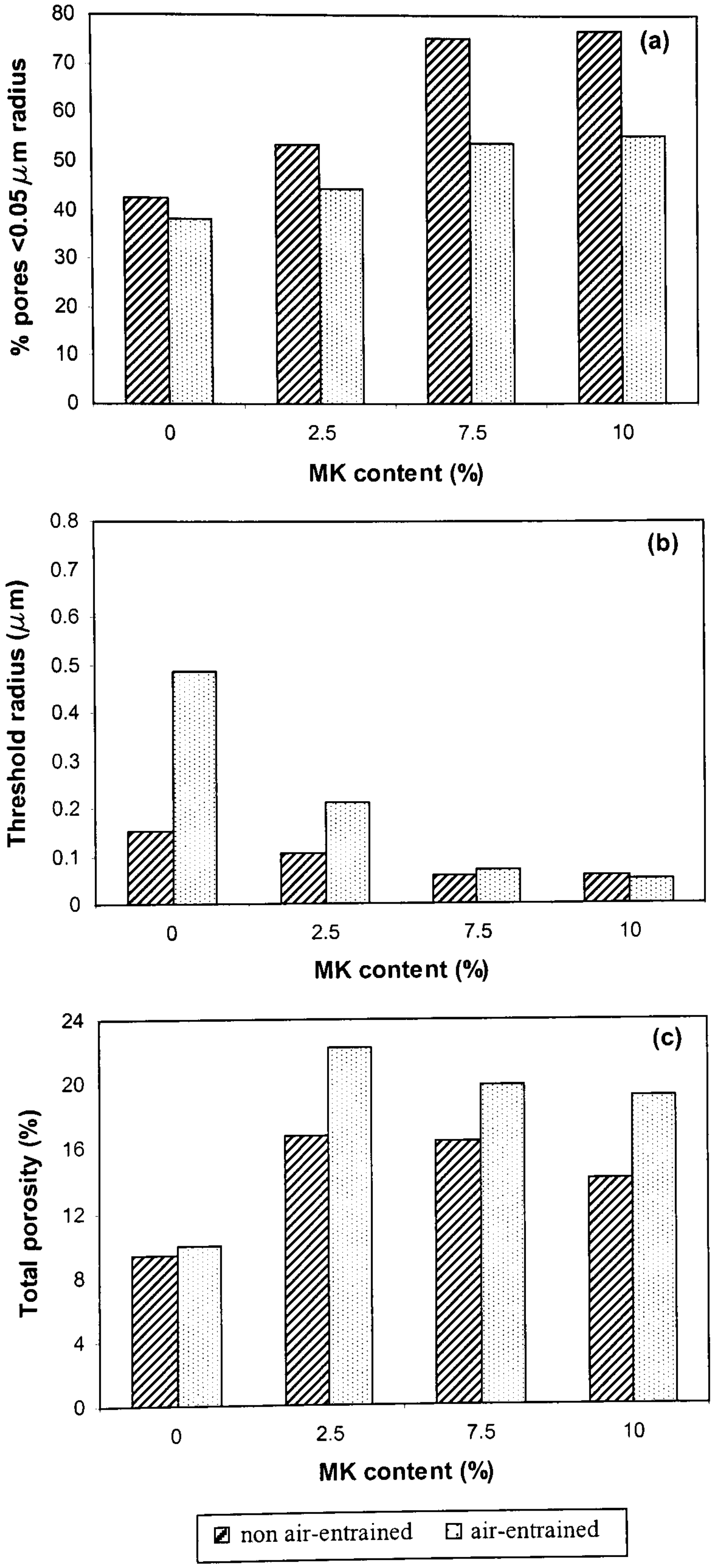


Figure 6.2 Influence of MK on (a) % of pores <0.05μm (b) threshold radius and (c) total porossity for non air-entrained and air-entrained concretes.

then decreases with further increases in MK. In addition it can be seen that the presence of air in concrete, regardless of the MK replacement level, has the effect of significantly increasing the total porosity of the concretes, although the effect is small in the case of the control concrete. It seems that a portion of the air voids present in the air-entrained concrete (diameters > 5 μm) are intruded by mercury, thus giving increased porosities with respect to the non air-entrained concrete. The pore refinement caused by the MK is associated with improvement in freeze-thaw performance exhibited in Figure 5.13 and scaling resistance in Figure 5.15.

Fly Ash concrete

Figure 6.3 gives the MIP results for the control and FA concretes. The numerical data are given in Tables D4-D6. Figure 6.6(a) clearly shows that whether or not air is entrained into the system, FA does not produce the pore refinement produced by MK as shown in Figure 6.2(a). Although, as in the case of MK concrete (Figure 6.2(a)), air entrainment appears to give rise to an increase in the value of threshold radius in the FA concrete (Figure 6.3(b)) in both air-entrained and non air-entrained concretes, the systematic reductions caused by increasing MK content is not shown by the FA concretes as FA content is increased. The influence of FA on the threshold radius appears to be dependent on whether or not air is entrained. Whereas in the air-entrained concrete, FA causes a decrease in the threshold radius, the non air-entrained concretes show increases caused by FA. These results (Figure 6.3(b)) demonstrate that the detrimental effects brought about by the FA may be obviated, and indeed reversed, if air entrainment is employed. This observation is further consolidated by the results for total porosity of the FA concretes. (Figure 6.3(c)), which show small reductions caused by air-entrainment. It is to be pointed out, however, that as with MK concretes, the total porosity is increased by the incorporation of FA.

Concrete at 10% total replacement level

Figure 6.4 compares the results of the control concrete and concretes incorporating FA, MK and a blend of FA+MK at 10% total PC replacement level. While the replacement of PC by 10% FA results in a negligible decrease in the percentage of

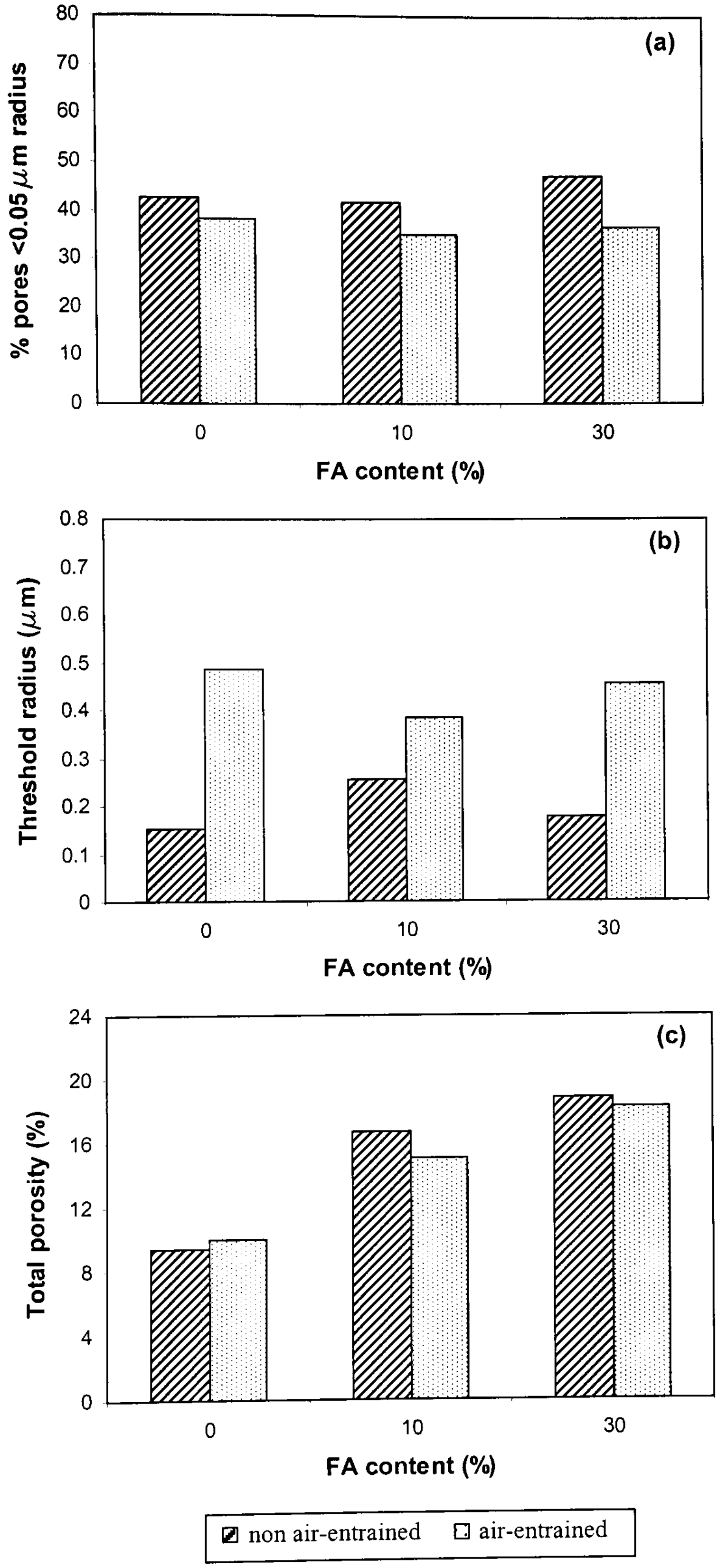


Figure 6.3 Influence of FA on (a) % of pores <0.05μm (b) threshold radius and (c) total porossity for non air-entrained and air-entrained concretes.

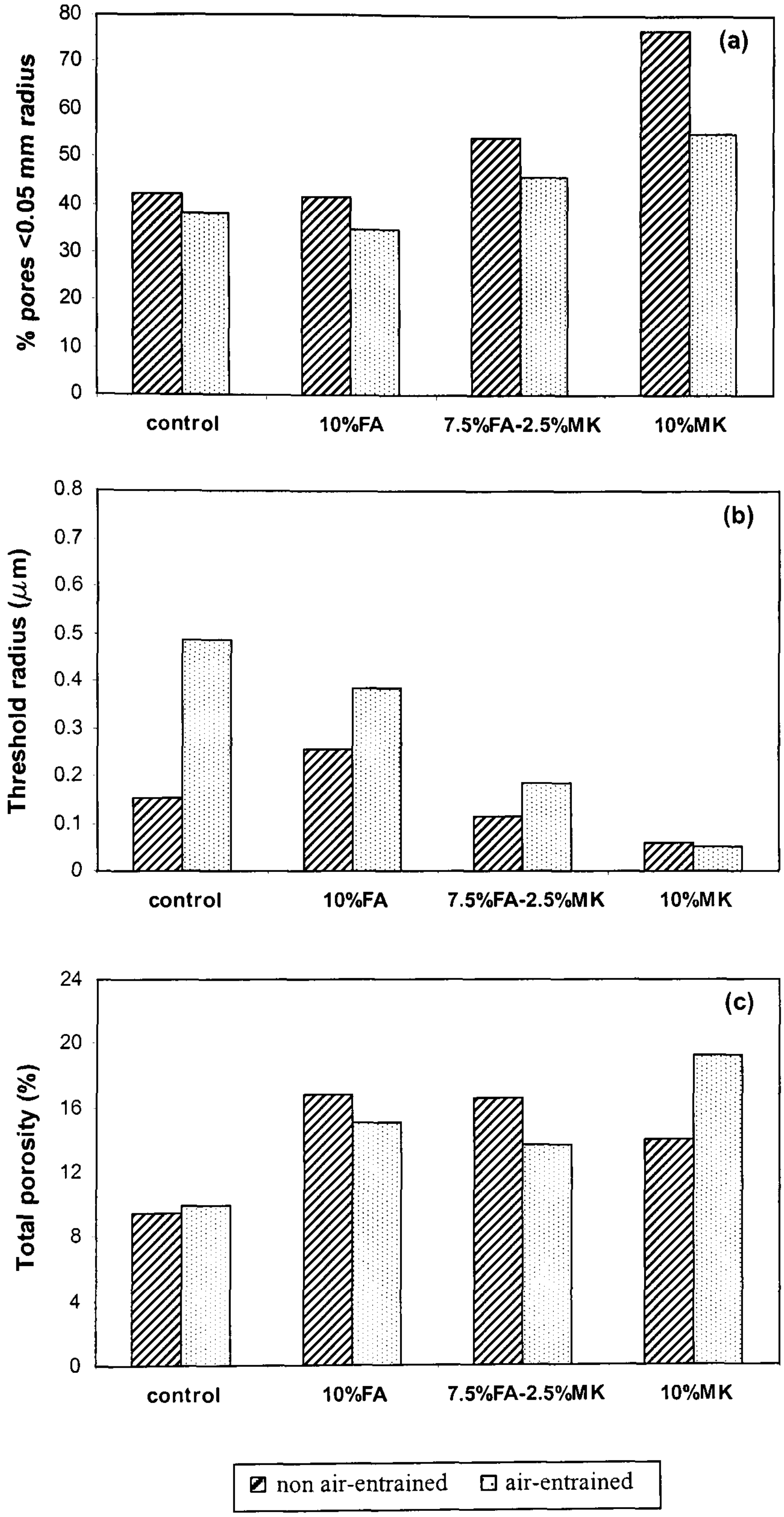


Figure 6.4 Influence of pozzolans at 10% total replacement level on (a) % of pores <0.05μm (b) threshold radius and (c) total porossity for non air-entrained and air-entrained concretes.

total volume made up of pores finer than 0.05 μm, the results indicate that, irrespective of whether the concrete is air-entrained or not, the incorporation of MK causes a refinement of the pores. This pore refinement caused by the presence of MK is also manifested in the threshold radius results. Although the FA concrete showed higher values of threshold radius as compared to the control concrete, the replacement of 25% of FA by MK (MK:FA = 1:3) has the effect of reducing the threshold radius to a value below that of the control. Further reduction is observed in the case of the binary 10% MK concrete. As with the 10% FA of MK concretes, the ternary 7.5%FA-2.5%MK concrete also shows increase in total porosity over that of the control.

<u>Concrete at 30% total replacement level</u>

Figure 6.5 gives a comparison of the MIP results for the control, binary FA and ternary FA-MK concretes at 30% total PC replacement level. The replacement of 25% of the FA by MK (MK:FA = 1:3) in the 30%FA non air-entrained or air-entrained concrete causes pore refinement as indicated by the increase in the percentage of the total pore volume which is made up from pores of radii < 0.05 μm, Figure 6.5(a), and the decrease in the threshold radius, Figure 6.5(b). However, as in the case of the 10% binary blend (Figure 6.4(c)), this replacement has no apparent effect on the total porosity of concrete (Figure 6.5(c)). In addition, as was the general observation made earlier from Figures 6.2, 6.3 and 6.4, total porosity increased as the PC is replaced by pozzolans.

6.2 Sorptivity and water absorption

6.2.1 Experimental techniques

Capillary suction (sorptivity) data are greatly influenced by the initial moisture content of the specimen under test. For this reason a consistent and systematic method of drying was applied to all samples before testing for sorptivity. The concrete discs were dried to constant weight in a temperature controlled drying cabinet containing silica gel. The dehydration of the C-S-H gel, the major hydration

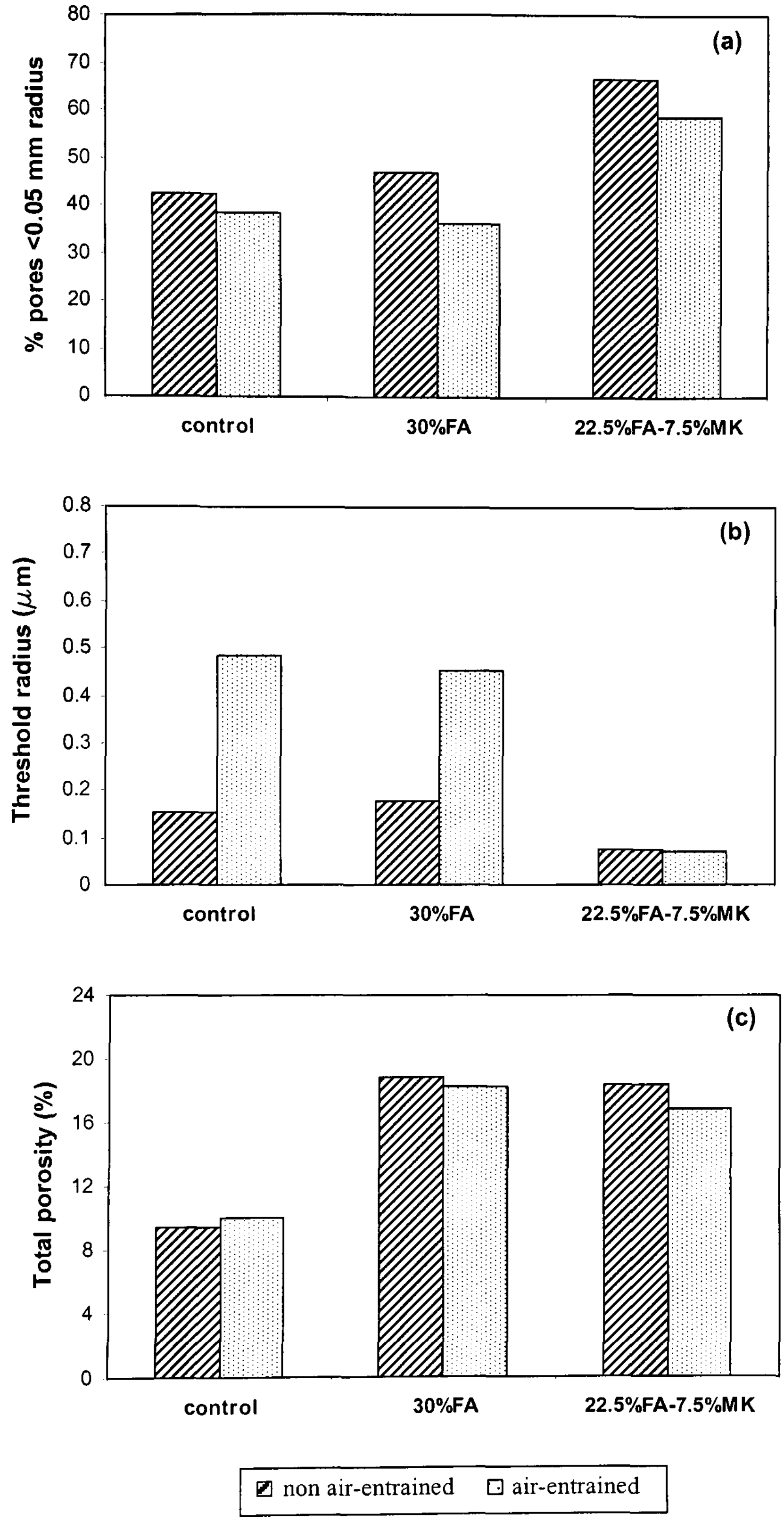


Figure 6.5 Influence of pozzolans at 30% total replacement level on (a) % of pores <0.05μm (b) threshold radius and (c) total porossity for non air-entrained and air-entrained concretes.

product of PC paste, can damage the microstructural features, which can affect properties such as sorptivity. For this reason the temperature for drying was kept low at 40°C. Sorptivity is also strongly influenced by carbonation. Generally carbonation causes reduction in sorptivity, particularly in the case of air-cured concrete [Dias, 2000]. Thus, a carbosorb agent was present in the drying cabinets to avoid carbonation and hence alteration of the sorptivity results. Drying was stopped when four consecutive weight loss readings resulted in mass change of less than 0.01%. Typical plots of weight loss versus drying time of top samples (see Figure 3.10) for the non air-entrained mixtures examined in this study are given in Figure 6.6. It is seen that, the time required to achieve constant weight varied between 55 and 65 days, depending on the pozzolan used. It is also seen that concretes incorporating FA had greater losses in weight, especially at the initial stages of drying. This suggests that more free water is remaining for pozzolanic reaction in the FA concretes, because of the slow reaction of FA particles. Also a more open structure enables that water to evaporate more rapidly. It is also noted that irrespective of the pozzolan used most of the water is lost at around 30 days of drying. During this period hydration is still continuing. Thus sorptivity values could be decreased as a result of continued hydration during drying.

It has been shown [Hall, 1989] that during the initial absorption period of a mortar or concrete surface exposed to wetting there exists a linear relationship between the cumulative water absorption i, and the square root of elapsed wetting time t of the form:

$$i = S\sqrt{t} \qquad [6.2]$$

where S is the sorptivity measured in g/mm^2 (of wetted area) per min$^{1/2}$. It is easily determined from the slope of the linear part of the i versus $\sqrt{t}$ plot.

The sorptivity tests were conducted using an apparatus developed by Sabir et al. [1998] which was described in Chapter 3. Typical plots of cumulative water absorption against the square root of time from 16 to 64 minutes of testing are shown

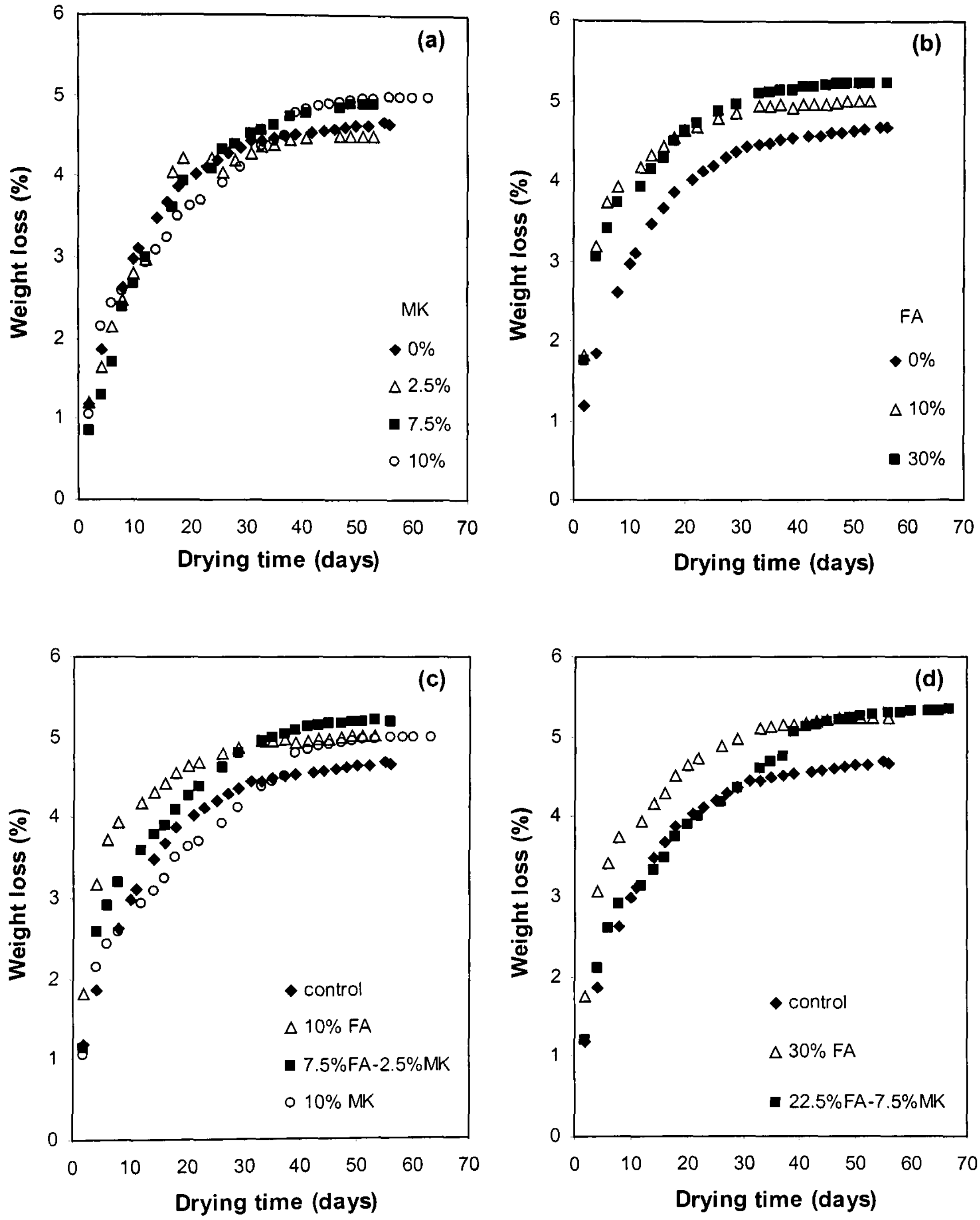


Figure 6.6 Weight loss due to drying for non air-entrained concrete samples used for sorptivity tests containing various amounts of (a) MK (b) FA and pozzolans at (c) 10% and (d) 30% total replacement level.

in Figure 6.7. These plots give the water absorption rate for the non air-entrained concretes containing MK, FA or blends of FA and MK at different replacement levels. Each plot shown refers to one of the two samples tested from each mixture. For this time period all the samples tested gave correlation coefficients greater than 0.99. The mean slopes of such plots for all mixtures investigated (two samples each) are given in Tables D.9 to D.16 in Appendix D. For the majority of samples tested in this investigation, the relationships between cumulative water absorption by capillary suction and the square root of time showed high linearity for the whole time of testing, i.e. 1 to 64 minutes. However it was found that the sorptivity calculated based on the first 16 minutes is consistently lower than that obtained from the data between 16 and 64 minutes (see Table D.9 to D.16). This can be attributed to buoyancy effects occurring at the beginning of testing, although the water reservoir was sufficiently large to ensure that any changes in buoyancy of the specimen undergoing testing were negligible. In practice the point of origin, and frequently the very early readings, are omitted when determining the slope of the graph. This is because there is an increase in the mass of the specimen caused by the filling of the open surface pores on the inflow surface and the sides of the specimen when is submerged. In order to reduce these effects to a minimum, it is essential that the specimen be submerged in water to no more than 2-5 mm [Neville, 1995]. For this reason in adopting a systematic methodology for determining the sorptivities for the various mixtures it was decided to base the calculations on the time between 16 and 64 minutes and it is these results that are reported here.

The disc specimens used for sorptivity tests were reconditioned, by drying in a dessicator at 40°C using silica gel, for use in the water absorption tests. Typical plots of the weight loss during this reconditioning for the samples presented in Figure 6.6 are given in Figure 6.8. As might be expected, irrespective of the pozzolan used, the water loss due to drying when the samples are reconditioned is generally less than that lost when dried the first time, and the duration of drying is generally less.

The dry samples of known dry mass are fully immersed in a tank of water at 20 ± 1°C and after 24 hours are removed from the water and the wet mass is taken. The

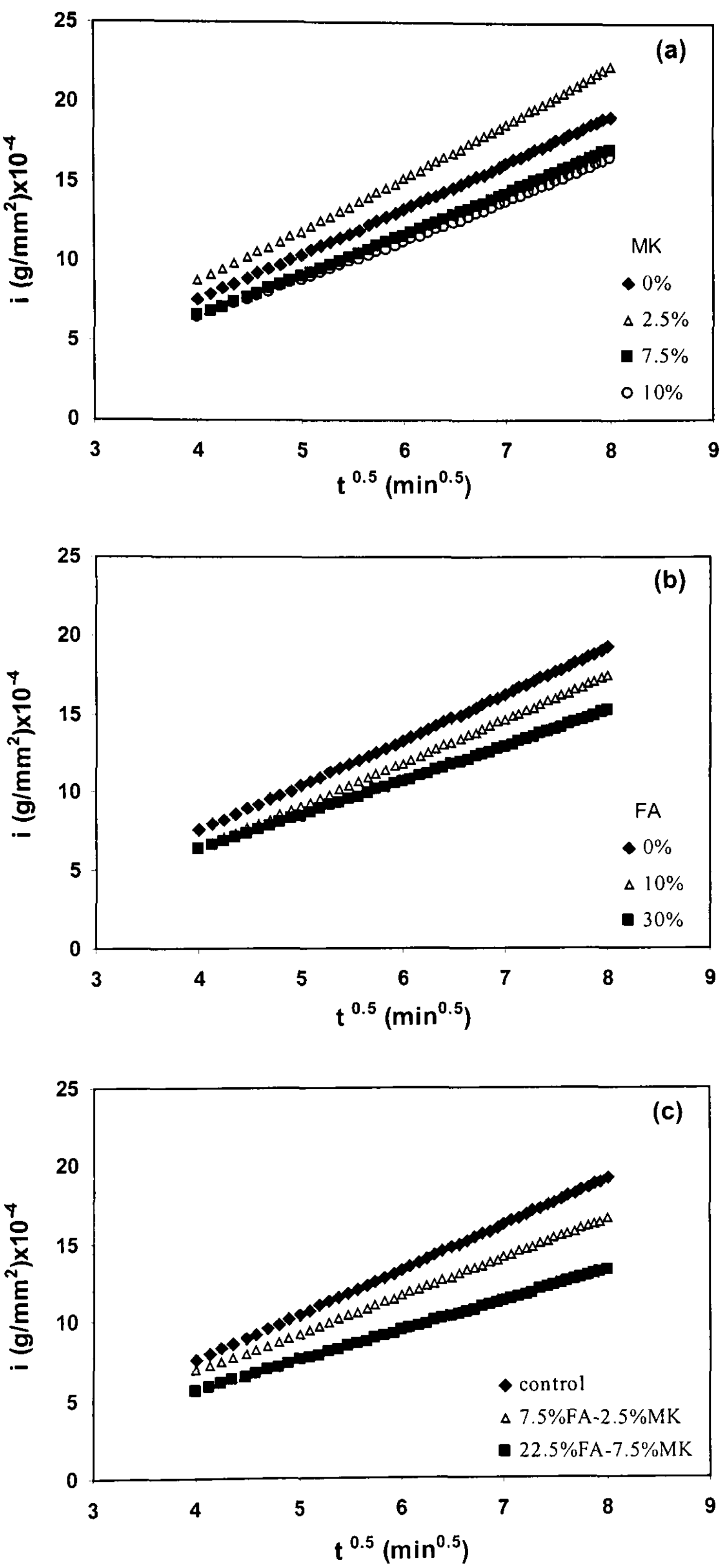


Figure 6.7 Cumulative water absorption by capillary suction for the non air-entrained concretes containing various amounts of (a) MK (b) FA and (c) blends of FA and MK.

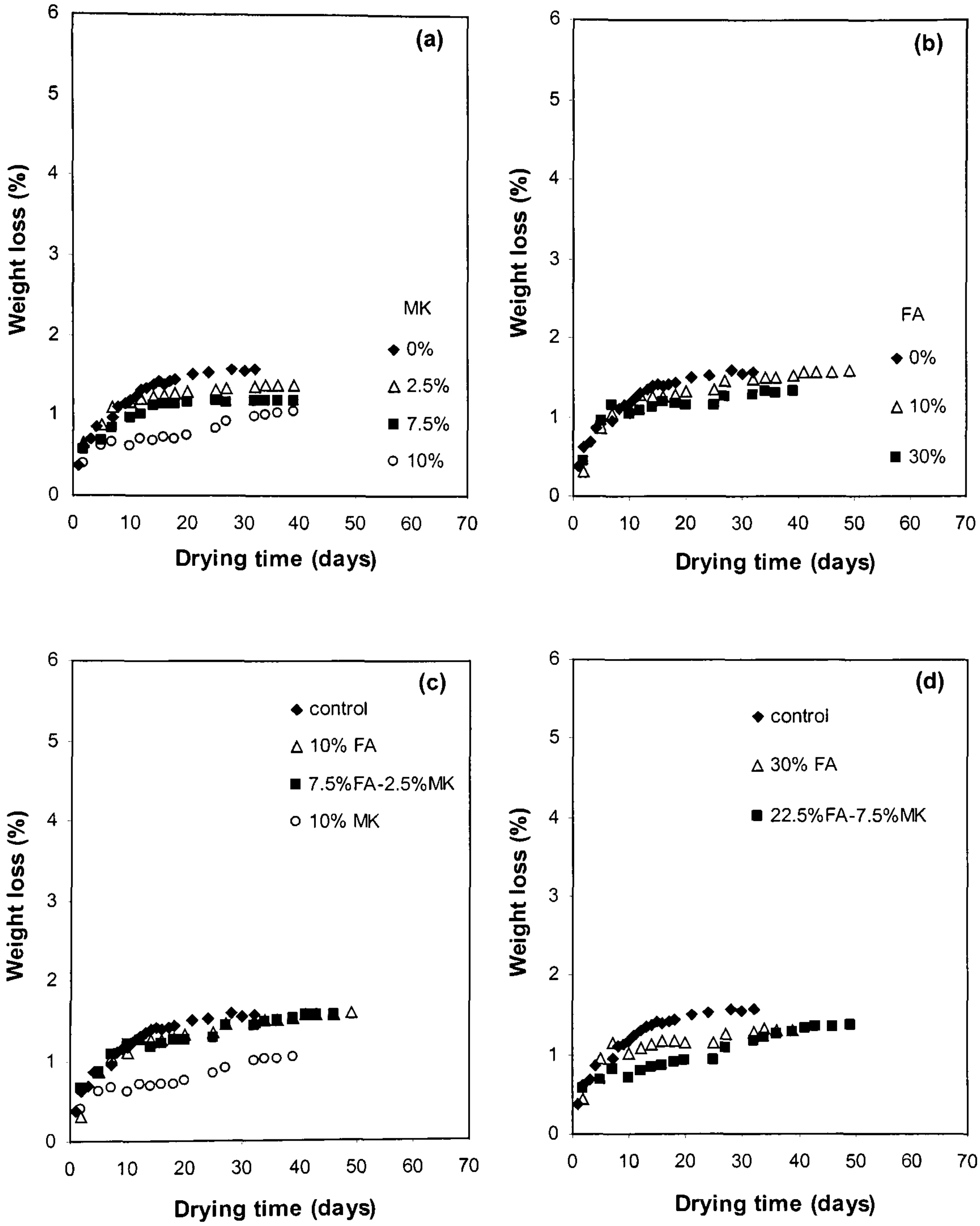


Figure 6.8 Weight loss due to drying for non air-entrained concrete samples used for water absorption tests containing various amounts of (a) MK (b) FA and pozzolans at (c) 10% and (d) 30% total replacement level.

total water absorption, W, of the material is usually expressed as a percentage of the mass of the dry mass of the sample and is calculated from:

$$W = \left(\frac{wet\ mass - dry\ mass}{dry\ mass} \right) x100 \qquad [6.3]$$

6.2.2 Results and discussion

Metakaolin concrete

The change in sorptivity with increasing replacement of PC by MK for non air-entrained and air-entrained concretes is given in Figure 6.9. Values of sorptivity can be found in Appendix D. It is apparent that irrespective of whether or not air entrainment is employed the sorptivity systematically decreases with increase in MK content. As with pore refinement (Figure 6.2(a)) the air entraining admixture appears to act in harmony with the MK in further reducing sorptivities. This is an indication that the pore refinement caused by MK (Figure 6.2) is accompanied by a reduction in the volume of interconnected capillaries caused by the filling effects of MK and gel formation caused by the pozzolanic reaction of MK with CH. Figure 6.10 shows that the total water absorption is slightly increased by the introduction of MK into the system. This increase, however, is not surprising as the total porosity as determined by MIP also increases (see Figure 6.2(c)). It should be noted that the water absorption represents the total open porosity of the specimens, whereas sorptivity represents a suction rate by which capillary pores take up water. These two parameters therefore represent different material characteristics. Sorptivity is much more dependent on pore structure as opposed to total open porosity. For specimens with identical pore structure and pore size distributions one would expect sorptivity to increase with increase in total absorption. However for specimens of different pore structure and pore size distribution it is quite possible for sorptivity to decrease whilst the water absorption increases.

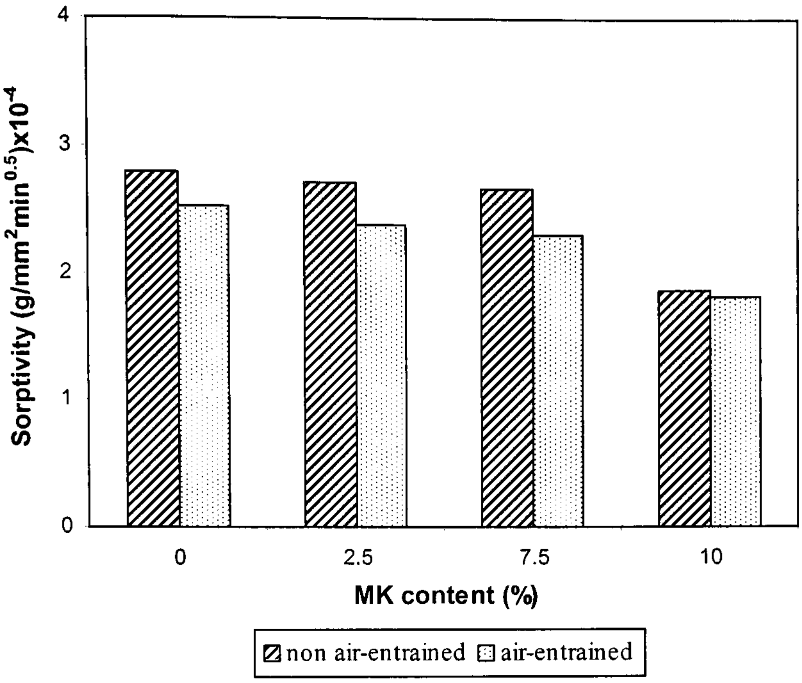


Figure 6.9 Influence of MK on sorptivity of non air-entrained and air-entrained concretes.

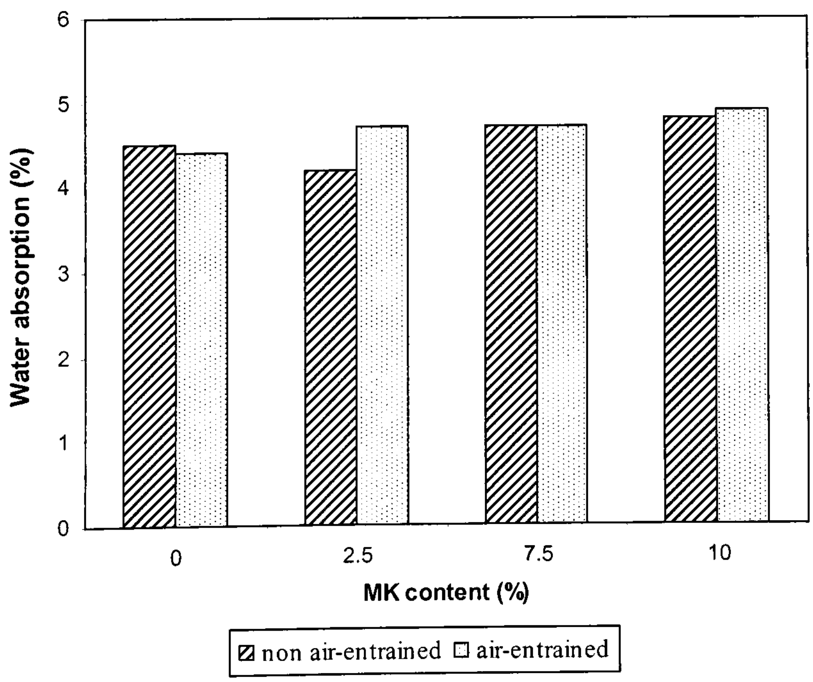


Figure 6.10 Influence of MK on water absorption of non air-entrained and air-entrained concretes.

Fly Ash concrete

Figures 6.11 and 6.12 give the results for the sorptivity and total water absorption for the FA concretes. As with MK concrete systematic reductions in sorptivity are achieved by the incorporation of FA, particularly in the non air-entrained concretes. Further reductions in sorptivity are generally produced by air entrainment. Again, as with MK, Figure 6.12 shows increasing water absorption with increasing FA content. A comparison of Figures 6.9-6.12 shows a somewhat more open structure in the case of the FA concrete as compared to that of the MK concrete.

Concrete at 10% total replacement level

The sorptivity and water absorption values for the PC concrete and PC-FA, PC-FA-MK and PC-MK concretes at 10% total replacement level, are compared in Figures 6.13 and 6.14. It is observed that concretes containing pozzolans have lower sorptivities and somewhat greater water absorptions than those of the control. It is also seen that the incorporation of MK produces a much more pronounced decrease in sorptivity than FA at the same replacement level. These results are consistent with those obtained by the MIP tests.

Concrete at 30% total replacement level

Figures 6.15 and 6.16 give the results for the concretes with 30% total PC replacement by FA or FA and MK. The results again demonstrate the effectiveness of MK in reducing sorptivity whether or not air entrainment is applied. However, water absorption tends to increase slightly by the incorporation of FA or blends of FA and MK.

6.3 Concluding remarks

The results presented in this chapter give a description of the microstructure of the concretes under investigation based on MIP and water absorption data. The specimens examined were obtained from cubes cast from the same mixtures used for making the specimens used for freeze-thaw testing. These related to concretes in which the PC was partially replaced by various compositions of FA and MK. For the ternary mixtures the MK:FA ratio was kept constant at 1:3. The maximum contents

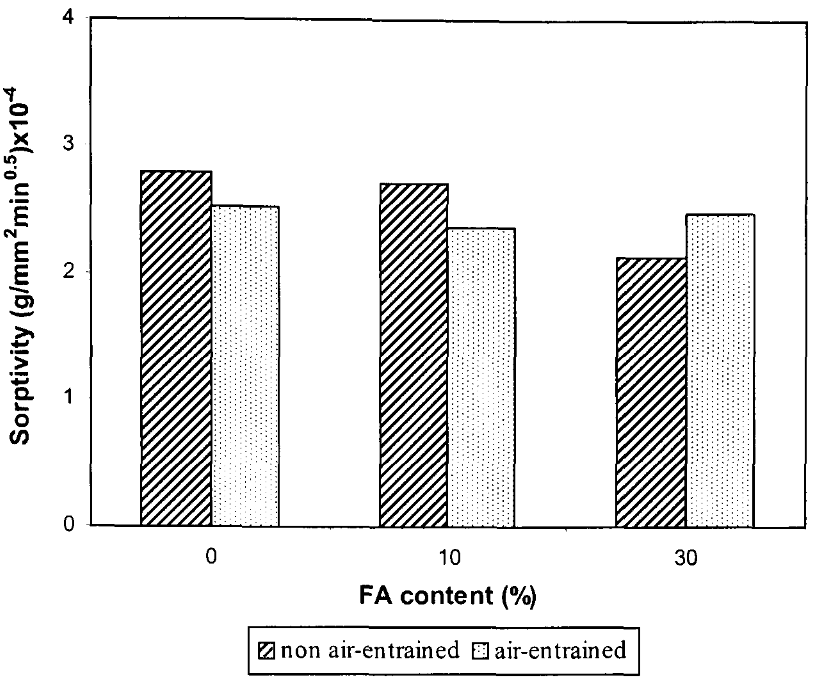


Figure 6.11 Influence of FA on sorptivity of non air-entrained and air-entrained concretes.

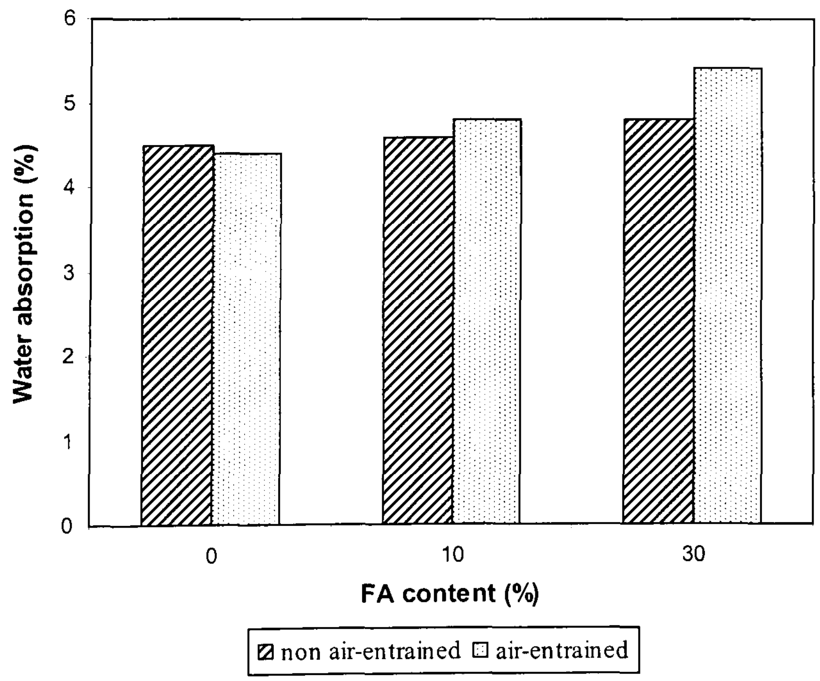


Figure 6.12 Influence of FA on water absorption of non air-entrained and air-entrained concretes.

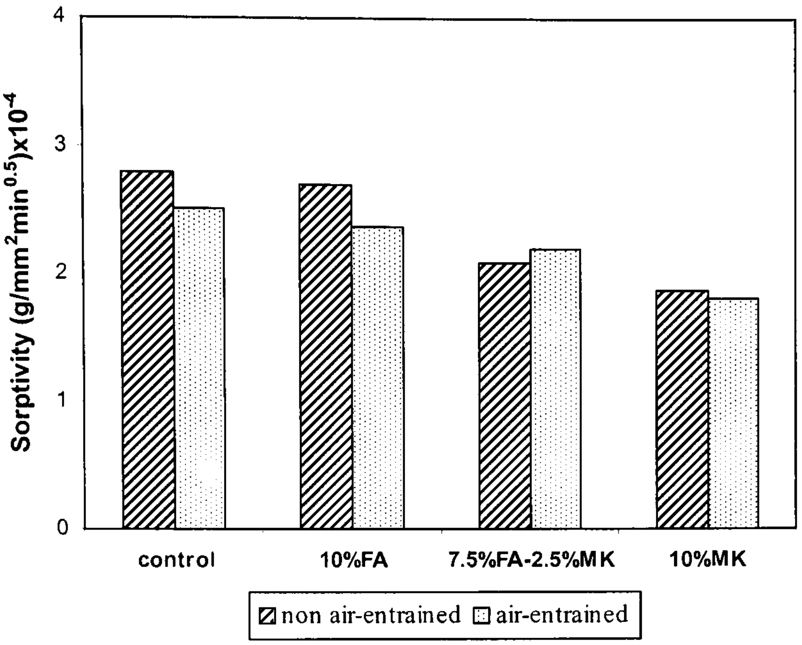


Figure 6.13 Comparison of sorptivities of non air-entrained and air-entrained. control concretes and concretes incorporating pozzolans at 10% total replacement.

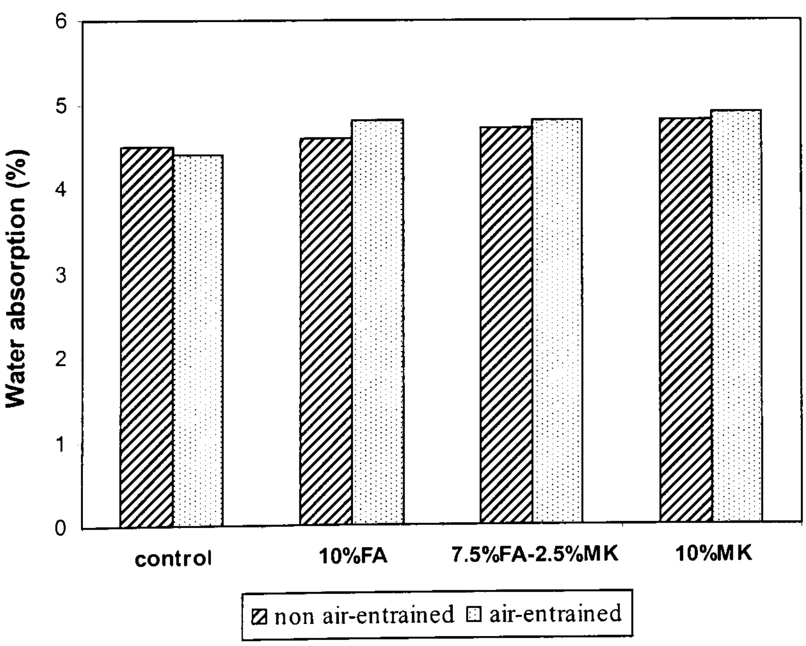


Figure 6.14 Comparison of water absorption values of non air-entrained and air-entrained. control concretes and concretes incorporating pozzolans at 10% total replacement.

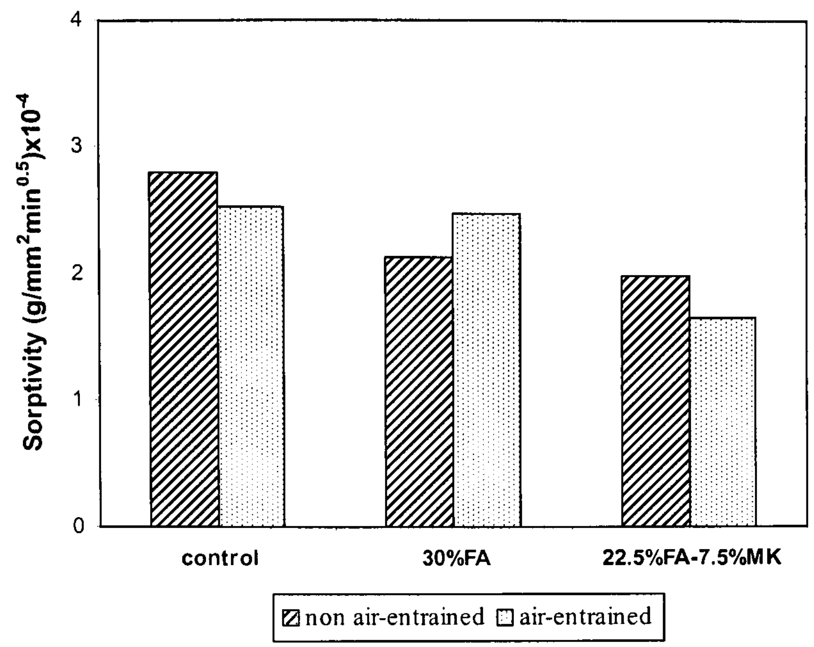


Figure 6.15 Comparison of sorptivities of non air-entrained and air-entrained. control concretes and concretes incorporating pozzolans at 30% total replacement.

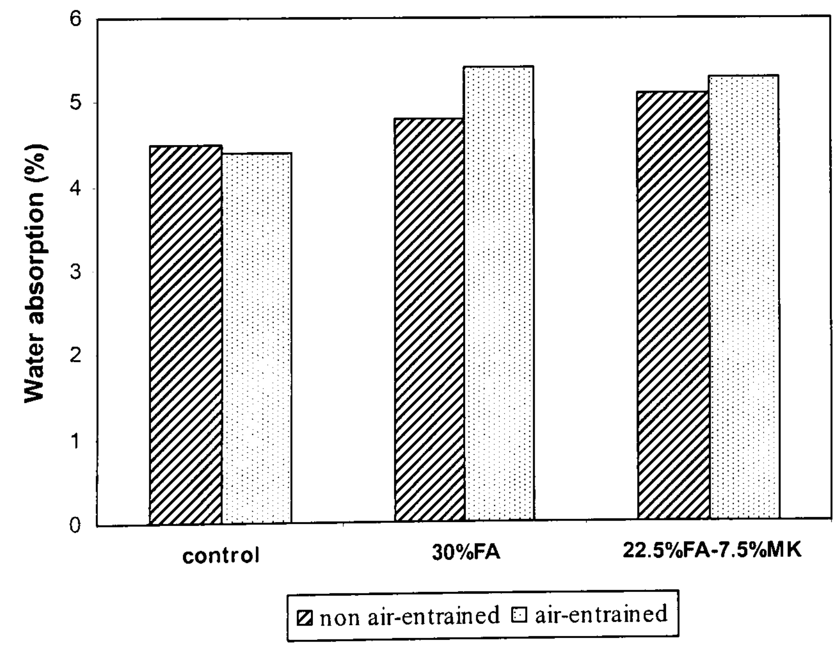


Figure 6.16 Comparison of water absorption values of non air-entrained and air-entrained. control concretes and concretes incorporating pozzolans at 30% total replacement.

of MK and FA employed were 10 and 30% respectively. It was found that binary PC-MK blends result in significant pore refinement, particularly when air entrainment is not employed. This refinement was demonstrated by both the % of the pore volume intruded via pores < 0.05 μm in radius and by the values of threshold radius. The limiting pore size for micropores was taken as pore radius of 0.05 μm and this corresponds to the reported size of the largest of the C-S-H gel pores. It is generally assumed that gel pores are too fine to transmit water by capillary action and the results obtained for the sorptivity of MK concretes confirm this. Although, the total porosity as observed by the MIP data, was found to increase by the incorporation of MK, its value decreased with increasing MK content. However as might be expected the total intruded pore volume increased when entrained air was incorporated (Figure 6.2(c)).

Pore refinement was also exhibited by the concrete mixtures containing FA, although the improvement was not as great as that for the MK concretes. For the air-entrained FA concrete, rather unexpected, the total intruded pore volume is generally less than for non air-entrained concrete. The introduction of MK into the ternary blends in the ratio MK:FA of 1:3 makes significant improvements in the pore structure over that of the control and binary FA concrete.

The results for the sorptivity and water absorption tests were generally reinforced by the MIP data. In all cases pore refinement effected by the pozzolans corresponded with decrease in sorptivity. Small increases in water absorption were detected due to increasing pozzolan content. These did not correspond well with the significant increases in total porosity as determined by MIP data. A reason for this could be the presence of the aggregates which might be causing a decrease in the total porosity but at the same time an increase in the water absorption as water can be absorbed not only by the paste but also by the minute pores of the aggregates themselves.

Also an important feature to note is that irrespective of the pozzolanic material or blends of materials used the presence of entrained air appears to have a negative effect on pore refinement. However this observation is not reflected in the sorptivity results which could be an indication that the entrained air voids do not contribute to the absorption of water by capillary suction, maybe because they are too large (5 μm-1 mm in diameter) and discontinuous. On the other hand and as might be expected the presence of air would appear to cause an increase in the total porosity although the water absorption results suggest that air entrainment has little or no effect on water absorption.

Chapter 7- Discussion, conclusions and further work

This Chapter discusses the principal findings of the author's research and presents the conclusions that may be drawn from the results obtained. The author also suggests further research that will complement and build on the results presented in this thesis.

7.1 General discussion

The effects of air entrainment on slump, and air content of concretes containing SF, FA, MK or combinations of the two pozzolans formed the basis for the design of the mixtures to be used for the freeze-thaw investigations and further studies on porosity and water absorption. The AEA resulted in increased workability in both the SF and MK but the improvement in workability of MK concrete occurred for an increased range of dosages of air entraining agent as compared to that obtained for SF concrete. This was attributed to the coarser particle size of MK as compared to that of SF resulting in less admixture being adsorbed by the pozzolan and increased dispersal. Also at the same replacement level this increase in workability was higher in MK concrete suggesting lower water demand for MK concrete as compared to SF concrete. In the case of FA concrete improvements in workability occurred with increasing amount of FA but these were limited to a certain AEA dosage of up to 0.18% for all FA levels. When PC was replaced by blends of FA and MK with total PC replacements of 20, 30 and 40% it was found that the beneficial effects on workability due to the air-entraining agent are lost as the total replacement increases. In addition and as would be expected workability was systematically decreased as the MK content increased. It was also found that the reduction in slump when the PC is blended with MK and FA in the ratio 1:3, increases with increase in total replacement relative to the PC-FA concrete.

MK concrete exhibited steady increases in the air contents for AEA dosages up to 0.24%. This optimum limit was significantly greater than the limit of 0.12% dosage exhibited by the SF concrete. The results also indicated that it would be difficult to entrain air in excess of about 6%, (though normally not desirable) in 20% MK concrete even with high dosages of air entrainment agent whereas in the case of 10% MK, air contents in excess of 10% may be achieved. Similar results were encountered in the case of 10 and 20% SF concretes. The incorporation of FA caused large reductions in the air content, irrespective of the dosage of the air entrainment agent. This reduction increases as the FA level increases for all dosages of the admixture. Although moderate increases in air content were obtained for the 20% FA concrete, albeit at the cost of high dosages of the admixture, little or no gain in air content was exhibited by the 30 and 40% FA concretes. This is attributed to the absorption effects caused by the unburnt carbon that is normally present in FA.

Based on a criterion that unsatisfactory resistance to freezing and thawing corresponds to a DF less than 60% or a change in length greater than 200 μm/m it was found that irrespective of the pozzolan used or replacement level employed, the non air-entrained concretes performed poorly under freezing and thawing. However there was an indication that concrete containing 2.5% MK show enhanced resistance to freezing and thawing. The better performance of the 2.5% MK concrete can be well correlated to the increased total porosity of the concrete. The increased porosity coupled with a finer more segmented pore system could explain why the non air-entrained 2.5%MK concrete has greatly improved frost resistance. On the other hand, the poor performance of the non air-entrained FA or FA-MK concretes was a result of a more open structure as suggested by the gain of weight at the initial stages of the freezing and thawing testing for all the non air-entrained concretes incorporating FA or FA blended with MK (FA:MK = 1:3). Although the ternary FA-MK blend showed improvement over the binary FA concrete, this still gave inferior performance compared to that of the control concrete. It seems that the level of MK in the system is probably not sufficient to develop a greatly refined pore structure with which MK is normally associated. It is interesting to note, however, that the significant improvement in performance obtained in the case of the ternary blend of FA-MK obtained at the 10% total replacement level of PC was not replicated in a significant way in the case of the 30% replacement. Although this may be due to the high level of replacement of PC by FA and the associated reduction in pozzolanic activity up to the age of 21 days, it will be shown later that, in fact, the reduction in strength at 21 days due to the incorporation of 30% FA is eliminated by further blending with MK. This is further evidence that the resistance to freezing and thawing action cannot directly be related to the compressive strength and that such resistance is more directly influenced by the air-void system of the concrete. On the other hand, it was found that all the air-entrained concretes exhibited excellent performance under freeze-thaw conditions irrespective of the MK or FA content highlighting the importance of air entrainment to ensure good freeze-thaw performance.

Generally, irrespective of the pozzolans used, scaling shows great reduction when concrete is air-entrained. It was found that MK concretes at all replacement levels and whether air-entrained or not show reduced weight losses due to freezing and thawing over those of the control. In the case of FA concrete both the non air-entrained and air-entrained concretes show that the 30% FA concrete suffers more weight loss than the control or 10% FA concretes. Also the concrete incorporating 10% FA, whether air-entrained or not, exhibited more scaling than the control, MK and FA-MK concretes.

Irrespective of the pozzolan employed however (i.e. FA, MK or blend of FA with MK) the air-entrained concretes gave better air void parameters than those of the non air-entrained concretes. This explains the great improvement in the freeze-thaw performance of the air-entrained concretes over that of non air-entrained concretes reported earlier. For the non air-entrained control concretes the replacement of PC by MK or FA appears to cause an increase in the spacing factor value. However, no significant variation in the spacing factor was caused by the level of MK or FA in the system. These observations were supported by the results for the specific surface which show significant reductions in the cases of concretes incorporating MK or FA. These reductions again appear to be constant and unaffected by the MK or FA content. Although the spacing factor in the air-entrained concrete increases when

2.5% MK is incorporated in the mixture, increasing amounts of MK appear to lead to reductions in the values of spacing factor. This reduction in spacing factors correlate well with the measured values of the specific surface, which show an increasing trend as the MK content increases. In the case of the air-entrained FA concrete, the role played by FA in affecting the measured parameters is not consistent. It is to be emphasized that the incorporation of FA necessitated the addition of greater volumes of air-entraining agent in order to achieve the required air content (6%). Despite the achievement of the required air content, it appears that the interaction between the FA particles and the air-entraining agent is somehow erratic and does not lead to systematic changes in air-void parameters with respect to increasing FA content.

It is apparent that irrespective of whether or not air entrainment is employed the sorptivity systematically decreases with increase in the MK content. As with pore refinement the air entraining admixture appears to act in conjunction with MK in further reducing sorptivity. This is an indication that the pore refinement caused by MK is accompanied by a reduction in the volume of interconnected capillaries caused by the filling effects of MK and gel formation caused by the pozzolanic reaction of MK with CH. It is also found that the total water absorption is slightly increased by the introduction of MK into the system. This increase, however, is not surprising as the total porosity as determined by MIP also increases. As with MK concrete, systematic reductions in the sorptivity are achieved by the incorporation of FA, particularly in the non air-entrained concretes. Further reductions in sorptivity are generally produced by air entrainment. Again, as with MK concrete, increasing water absorption with increasing FA content are observed. A comparison of the two shows a somewhat more open structure in the case of the FA concrete as compared to that of the MK concrete. It is observed that the concretes containing the pozzolans have lower sorptivities and somewhat greater water absorptions than those of the control. It is also seen that the incorporation of MK produces a much more significant decrease in sorptivity than FA at the same replacement level. These results are consistent with those obtained by the MIP tests. The results again demonstrate the effectiveness of MK in reducing the sorptivity whether or not air entrainment is applied. However, water absorption tends to increase by the incorporation of FA or blends of FA and MK.

7.2 Conclusions

The following conclusions may be drawn from the work described in this thesis:

- For a given slump and air content, concrete with SF has a greater superplasticiser requirement than equivalent concrete with MK, and for a given air content SF produces more demand for air-entraining admixture than MK. This is attributed to the greater surface area of the SF particles with consequent higher adsorption of the admixture by the very fine SF particles. In addition the superplasticiser enhances the performance of the air-entraining admixture and/or itself plays a secondary role in entraining air to the fresh concrete.

- The increase in the workability attributed to the air-entraining admixture is greater in MK concrete than in SF concrete. Also the improvement in workability of MK concrete occurs for a greater range of dosages of the admixture. This is attributed to the smaller specific surface of MK with less of the admixture being adsorbed. In the case of FA concrete the increase in slump due to the air-entraining admixture (up to 0.18%) occurs only in concretes with low levels of FA (20%). Concretes with 30 and 40% FA, although more workable, accrue no such benefit. The workability of FA-MK concrete is substantially reduced with increasing MK level at all total replacement levels, 20, 30 and 40%.

- FA causes large reductions in the air content of fresh concrete, irrespective of the dosage of the air-entraining admixture. This is attributed to the presence of unburnt carbon.

- MK concrete only provides strength enhancement up to 14 days, and beyond 14 days the effect of that enhancement is diminished whereas for SF concrete, particularly at high levels of replacement (20%) strength enhancement, although very considerable at 14 days still continues up to 90 days. FA concretes exhibited greater potential for increased strength at extended ages as compared to SF and MK. Considerable enhancement in compressive strength is achieved in the short and long terms when MK replaces part of the FA. Greater increases in the strength are obtained with increasing MK to FA ratios.

- Based on a criterion that unsatisfactory resistance to freezing and thawing corresponds to a DF of less than 60% or a change in length of greater than 200 μm/m, all the air-entrained concretes exhibited excellent performance under freeze-thaw conditions (DF > 90% at 120 cycles of freezing and thawing) irrespective of the MK or FA content, the only exception being the 30% FA concrete which showed a DF of 79% at 120 cycles. On the other hand, based on the same criterion the non air-entrained concretes performed poorly under freezing and thawing. Thus, it would appear that air entrainment is the controlling factor for good freeze-thaw performance and the material effects are less important.

- Non air-entrained concretes show great reductions in weight loss when PC is partially replaced by 2.5% MK. However, further additions of MK up to 10% leads to increase in weight loss. In contrast, the air-entrained concretes show a reduction in weight loss with increasing MK content from 2.5 to 10%, although the changes in weight loss due to different MK contents were small.

- Whether or not air entrainment is employed, high replacement levels of FA (30%) result in more scaling as compared to the control or 10% FA concrete, with the control exhibiting the least scaling. The poor performance of FA concrete as compared to the control concrete may be attributed to the slow pozzolanic reaction of the FA which results in (a) insufficient strength of the paste to resist cracking caused by the action of frost and (b) the development of a coarser pore structure.

- Air-entrained concrete containing FA or MK or combinations of them exhibited less surface scaling than the corresponding non air-entrained concretes. This underlines the importance of air entrainment in enhancing the ability of concrete to resist surface scaling induced by the action of frost.

- Whether air-entrained or not, FA with MK at an MK:FA ratio of 1:3 improves the scaling resistance of the concrete as compared to the FA only concrete. This improvement occurs at both the 10 and 30% total replacement levels. Non air-entrained concretes containing FA or blends of FA and MK show an increase in weight at the beginning of freezing and thawing, an indication of uptake of water due to a more porous matrix caused by the FA and suggests that the level of MK in the system is probably not sufficient to develop the more closed porosity with which MK is normally associated.

- PC replacement by up to 10% MK appears to cause a significant increase in the spacing factor. This increase can be attributed to the fineness of the MK particles compared to PC particles. The small particles of MK act as fillers occupying some of the voids present in the paste, thus reducing their number and resulting in greater spacing factors. In general the influence of FA on these parameters was similar to that caused by MK because of the fineness of FA particles relative to that of PC. As might be expected the lower spacing factors were associated with higher specific surfaces and greater void frequencies. Paste content was not affected by the incorporation of pozzolans. It appears that the main factor controlling the paste content is the water/binder ratio which was kept constant at 0.65.

- For a given concrete there is a linear relationship between the durability factor and expansion. This close correlation provides very strong evidence that the cause of expansion also leads to a decrease in the DF. For all non air-entrained concretes there is also a strong correlation between expansion and weight loss due to freeze-thaw action. This indicates that the basic mechanisms responsible for scaling are not very different from those causing expansion and thus internal cracking. Therefore the tensile stresses generated by the action of frost can cause cracking and loss of small paste particles at the surface of the concrete.

- For all concretes, the pore refinement effected by the pozzolans was associated with decreased sorptivity. On the other hand small increases in water absorption, due to increasing pozzolanic content, did not relate to the significant increase in total porosity.

- Irrespective of the pozzolanic material used the presence of entrained air appears to have a negative effect on pore refinement. However this observation is not reflected by the sorptivity results which could be an indication that entrained air voids do not contribute to absorption of water by capillary suction.

7.3 Recommendations for further work

The work in this thesis has opened up a number of new questions many of which deserve further investigation. The role of MK or blends of MK with FA on air entrainment is still not well understood. Even FA, one of the widely researched pozzolans should be included in future research because of its erratic behaviour with air entraining agents. The research showed that different pozzolans in concrete produce different demands for superplasticizer and air-entraining agent to achieve specific values of air content and slump. Future research is also required to examine if these different demands are affecting the freeze-thaw performance of concrete.

This investigation has shown that non air-entrained concretes incorporating small amounts of MK are frost resistant. Further investigations should therefore be covered and using a wide range of different concrete mixtures to establish how widely applicable this is and whether there are potential commercial applications to improve concrete frost resistance. On the other hand large amounts of MK appear to be detrimental for scaling and frost resistance in the case of non air-entrained concrete. Thus what level of replacement of PC with MK would be acceptable to still maintain resistance to freezing and thawing?

The poor performance of the non air-entrained FA concrete underlines the need for more curing before exposure to the action of frost. The use of different pozzolans in concrete necessitates curing for different durations before being subjected to freezing and thawing, in order to achieve a less porous structure and enough strength to survive the action of frost. Hence further research is needed to identify minimum curing requirements for concretes incorporating different pozzolans which are subject to freezing and thawing.

There was clear evidence that FA concretes at high PC replacement levels, even if they are air-entrained, exhibit more scaling than concretes containing MK or blends of MK and FA. On the contrary it was found that the presence of MK in FA-MK blends could be beneficial as far as scaling is concerned. For this reason the investigation of high volume FA concretes blend with small amounts of MK could be the subject of further work. FA is abundant and cheap whereas MK production is limited and of high cost. Large quantities of FA and small amounts of MK are thus an economically desirable combination that needs to be addressed in future research. In addition, a possible continuation of this project could be the use of deicer salts in testing of the above concretes. Deicer salt scaling is now recognized as the most important frost problem in many countries with low-temperature winter conditions, because deicer chemicals generally excarcebate the problem of frost.

The results showed that the freeze-thaw performance declined at spacing factors above 400 μm, except in the cases of non air-entrained concretes incorporating 2.5 and 7.5% MK. This would suggest that higher values of spacing factor can be tolerated by MK concretes to still ensure freeze-thaw durability. A study to investigate if this is true could be of practical significance if MK concrete becomes more widely used. Furthermore, it would appear that the air-entrained concretes with high percentages of FA, in this case 30%, are less durable than the other air-entrained concretes, possibly suggesting that reduced spacing factors are required at this replacement level to ensure enhanced freeze-thaw durability. However, given the limited data, the above observation warrant further testing for confirmation.

Finally more research is required to understand clearly the internal structure of concretes of different formulations especially those incorporating MK or combinations of FA with MK. In the current study pore refinement and porosity data obtained through MIP failed to indicate any clear relationship to freeze-thaw performance. The option of using MIP measurements at the end of freeze-thaw testing would enable the changes brought about to the pore structure by the freeze-thaw action to be investigated. The author also suggests that more experimentation with low temperature calorimetric results could be an option to see how the ice is formed within the concrete's structure containing different pozzolans.

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Appendix A Workability, air content and compressive strength data

Table A.1 Effect of SF and MK on the dosage of air entraining agent needed to give an air content of about 7.5% for a fixed SP (AF) content.

Material	*Mixture ref.*	*AF/b (%)*	*AE3/b (%)*	*Slump (mm)*	*Air content (%)*
SF	CON 35/06	0.35	0.06	210	7.3
	5S 35/09	0.35	0.09	120	7.8
	10S 35/25	0.35	0.25	80	8.0
	15S 35/40	0.35	0.40	60	7.6
	20S 35/99	0.35	1.00	45	7.3
MK	CON 35/06	0.35	0.06	210	7.3
	5M 35/06	0.35	0.06	120	6.9
	10M 35/15	0.35	0.15	105	7.6
	15M 35/35	0.35	0.35	90	7.3
	20M 35/85	0.35	0.85	50	7.2

Table A.2 Effect of SF and MK on the dosage of superplasticizer needed to give an air content of about 6% to a fixed AE3 content.

Material	*Mixture ref.*	*AE3/b (%)*	*AF/b (%)*	*Slump (mm)*	*Air content (%)*
SF	CON 31/06	0.06	0.31	85	5.0
	5S 43/06	0.06	0.43	100	6.0
	10S 63/06	0.06	0.63	115	6.0
	15S 78/06	0.06	0.78	100	6.2
	20S 86/06	0.06	0.86	110	6.1
MK	CON 30/06	0.06	0.30	85	5.0
	5M 35/06	0.06	0.35	120	6.9
	10M 50/06	0.06	0.50	110	6.0
	15M 65/06	0.06	0.65	120	6.2
	20M 80/06	0.06	0.80	115	6.9

Table A.3 Slump, compacting factor, air content and strength development of control and SF concrete.

Concrete	Mixture ref.	Slump (mm)	Compacting factor	Air content (%)	Compressive strength (N/mm^2)			
					7days	14days	28days	90days
Control	CON 30/00	85	0.91	2.9	52.6	58.2	65.2	74.3
	CON 30/06	85	0.97	5.0				
	CON 30/12	160	0.98	7.6	40.0	45.8	51.2	56.9
	CON 30/18	200	0.98	9.0	39.4	43.2	47.5	50.5
	CON 30/24	180	0.99	10.5				
	CON 30/30	210	0.99	11.2				
10% SF	10S 50/00	60	0.94	2.6	62.7	77.4	85.1	90.4
	10S 50/06	100	0.97	6.5				
	10S 50/12	105	0.98	8.0	45.0	55.5	61.9	65.7
	10S 50/18	115	0.98	9.0				
	10S 50/24	150	0.99	10.5	35.7	44.3	49.9	53.2
	10S 50/30	155	0.99	11.0				
20% SF	20S 50/00	5	0.85	2.8				
	20S 50/06	0	0.84	4.5				
	20S 50/12	15	0.89	6.8	50.6	64.7	75.9	81.8
	20S 50/18	35	0.89	5.5				
	20S 50/24	20	0.89	6.3				
	20S 50/30	45	0.91	7.5				

Table A.4 Slump, compacting factor, air content and strength development of control and MK concrete.

Concrete	Mixture ref.	Slump (mm)	Compacting factor	Air content (%)	Compressive strength (N/mm^2)			
					7days	14days	28days	90days
Control	CON 30/00	85	0.91	2.9	52.6	58.2	65.2	74.3
	CON 30/06	85	0.97	5.0				
	CON 30/12	160	0.98	7.6	40.0	45.8	51.2	56.9
	CON 30/18	200	0.98	9.0	39.4	43.2	47.5	50.5
	CON 30/24	180	0.99	10.5				
	CON 30/30	210	0.99	11.2				
10% MK	10M 50/00	75	0.93	2.5	60.1	73.2	79.1	81.4
	10M 50/06	140	0.95	6.5				
	10M 50/12	190	0.98	8.0	45.9	55.9	59.6	60.4
	10M 50/18	210	0.98	9.3				
	10M 50/24	collapsed	0.99	10.2				
	10M 50/30	collapsed	0.99	10.0	39.0	49.3	52.8	54.4
20% MK	20M 50/00	25	0.83	2.9	65.9	77.4	82.1	83.7
	20M 50/06	45	0.81	3.8				
	20M 50/12	55	0.86	4.5	58.4	70.3	73.6	77.2
	20M 50/18	60	0.87	5.5				
	20M 50/24	85	0.96	7.1				
	20M 50/30	95	0.95	7.3	49.1	58.3	62.4	67.2

Table A.5 Slump, compacting factor, air content and strength development of control and FA concrete.

Concrete	Mixture ref.	Slump (mm)	Compacting factor	Air content (%)	Compressive strength (N/mm^2)			
					7days	14days	28days	90days
Control	CON 30/00	85	0.91	2.9	52.6	58.2	65.2	74.3
	CON 30/06	85	0.97	5.0				
	CON 30/12	160	0.98	7.6	40.0	45.8	51.2	56.9
	CON 30/18	200	0.98	9.0	39.4	43.2	47.5	50.5
	CON 30/24	180	0.99	10.5				
	CON 30/30	210	0.99	11.2				
20% FA	20F 30/00	110	0.96	2.6	39.7	46.4	54.9	73.5
	20F 30/06	120	0.96	3.0				
	20F 30/12	150	0.97	3.1	35.9	42.7	48.6	63.9
	20F 30/18	200	0.99	4.7				
	20F 30/24	185	0.98	4.8				
	20F 30/30	190	0.98	6.5	32.4	36.5	41.6	55.2
30% FA	30F 30/00	160	0.96	2.5	33.1	38.8	47.6	64.8
	30F 30/06	175	0.97	2.8				
	30F 30/12	195	0.97	2.9	30.7	36.0	45.0	62.8
	30F 30/18	200	0.98	3.1				
	30F 30/24	205	0.98	3.4				
	30F 30/30	205	0.99	4.6	27.3	32.5	40.8	58.1
40% FA	40F 30/00	180	0.98	2.5	25.1	32.5	40.0	55.9
	40F 30/06	180	0.98	2.7				
	40F 30/12	180	0.98	2.9	24.2	30.9	39.1	54.9
	40F 30/18	185	0.98	2.9				
	40F 30/24	205	0.99	3.0				
	40F 30/30	210	0.99	4.3	24.1	31.1	37.9	50.9

Table A.6 Slump, compacting factor, air content and strength development of FA+MK concrete: 20% total replacement.

	Mixture ref.	Slump (mm)	Compacting factor	Air content (%)	Compressive strength (N/mm²)			
					7days	14days	28days	90days
FA:MK 1:1	10F10M 30/00	40	0.87	2.8	57.2	69.4	74.4	77.8
	10F10M 30/06	45	0.88	2.9				
	10F10M 30/12	55	0.91	3.2	53.3	65.1	70.0	72.6
	10F10M 30/18	65	0.92	4.4				
	10F10M 30/24	80	0.94	5.0				
	10F10M 30/30	100	0.97	7.2	43.3	54.0	55.4	59.4
FA:MK 3:1	15F5M 30/00	50	0.91	2.7	48.2	59.0	63.6	71.4
	15F5M 30/06	60	0.91	2.9				
	15F5M 30/12	75	0.94	3.1	45.9	54.8	59.6	69.0
	15F5M 30/18	95	0.95	3.4				
	15F5M 30/24	115	0.96	5.1				
	15F5M 30/30	150	0.98	6.5	37.8	47.5	51.8	58.3

Table A.7 Slump, compacting factor, air content and strength development of FA+MK concrete: 30% total replacement.

	Mixture ref.	Slump (mm)	Compacting factor	Air content (%)	Compressive strength (N/mm²)			
					7days	14days	28days	90days
FA:MK 1:1	15F15M 30/00	15	0.81	2.5	51.7	60.0	67.2	73.8
	15F15M 30/06	20	0.82	2.7				
	15F15M 30/12	20	0.82	3.0	52.9	63.2	67.5	70.9
	15F15M 30/18	25	0.82	3.1				
	15F15M 30/24	35	0.83	3.6				
	15F15M 30/30	35	0.83	4.6	47.5	55.7	61.6	62.5
FA:MK 3:1	22.5F7.5M 30/00	75	0.94	2.5	46.4	57.2	60.5	66.2
	22.5F7.5M 30/06	80	0.95	2.8				
	22.5F7.5M 30/12	75	0.95	2.9	44.4	54.6	57.8	65.6
	22.5F7.5M 30/18	85	0.95	3.0				
	22.5F7.5M 30/24	90	0.96	3.1				
	22.5F7.5M 30/30	105	0.97	4.1	40.3	49.7	53.4	56.7

Table A.8 Slump, compacting factor, air content, and strength development of FA+MK concrete: 40% total replacement.

	Mixture ref.	Slump (mm)	Compacting factor	Air content (%)	Compressive strength (N/mm^2)			
					7days	14days	28days	90days
FA:MK 1:1	20F20M 30/00	0	0.80	2.4	50.8	60.7	65.3	69.2
	20F20M 30/06	5	0.80	2.4				
	20F20M 30/12	15	0.81	2.3	48.7	59.5	63.9	67.5
	20F20M 30/18	15	0.81	2.4				
	20F20M 30/24	25	0.82	2.5				
	20F20M 30/30	25	0.84	2.8	48.6	57.8	62.0	65.7
FA:MK 3:1	30F10M 30/00	65	0.91	2.3	41.7	54.2	58.1	64.3
	30F10M 30/06	65	0.91	3.0				
	30F10M 30/12	80	0.92	2.6	39.7	52.4	57.7	61.8
	30F10M 30/18	75	0.93	2.8				
	30F10M 30/24	90	0.95	2.8				
	30F10M 30/30	95	0.95	3.0	37.5	49.8	53.6	59.5

Table A.9 Effect of increase in air content on reduction in compressive strength

Concrete	Air content increase (%)	Reduction in compressive strength (%)			
		7 days	14 days	28 days	90 days
Control	210	25	26	27	32
10% SF	304	43	43	41	41
10% MK	300	35	33	33	33
20% MK	152	25	25	24	20
20% FA	150	18	21	24	25
30% FA	84	18	16	14	10
40% FA	72	4	4	5	9

Appendix B Freeze-thaw and air-void system data

$^{\alpha}$ Specimen used for measurements in accordance with ASTM C666-92

$^{\beta}$ Specimen used for length measurements in accordance with BS 5075: Part 2: 1982

Table B.1 Freeze-thaw data for control concrete studied in series 1.

Mixture ref: *CON 20/12*							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	Resonant frequency (Hz)	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion ($\mu m/m$)*
0		7858	100	54.8	4.6		0
7	-0.01	7802	99	55.2	4.5	-0.02	-60
14	-0.09	7886	101	55.0	4.5	-0.03	-48
20	-0.12	7895	101	55.7	4.5	0.01	-36
30	0.00	7754	97	54.9	4.6	0.31	-8
37	0.12	7757	97	56.6	4.4	0.83	24
44	0.27	7620	94	58.0	4.3	1.30	4
51	0.51	7585	93	58.8	4.3	1.54	80
58	0.94	7401	89	58.2	4.3	1.81	88
64	1.21	7370	88	62.8	4.0	2.01	88
79	1.99	6948	78	62.3	4.0	2.63	224
93	2.52	5198	44	66.2	3.8	3.11	412
100	2.80	3525	20	69.5	3.6	3.44	440
107	2.93	3263	17	76.2	3.3	3.69	620
114	3.38	2527	10	81.1	3.1	3.97	800
124	3.93					4.38	1068

Table B.2 Freeze-thaw data for 10% SF concrete studied in series 1.

Mixture ref: *10S 30/12*							
	Specimen *A* [α]					Specimen *B* [β]	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8128	100	55.0	4.5		0
7	-0.01	8074	99	54.4	4.6	0.00	-84
14	-0.03	8062	98	54.3	4.6	-0.06	-108
20	-0.05	8070	99	55.0	4.6	-0.07	-116
30	0.09	8066	98	54.1	4.7	0.09	-192
37	0.11	8064	98	54.2	4.6	0.17	-88
44	0.19	8085	99	52.9	4.8	0.29	-148
51	0.24	8015	97	54.4	4.6	0.43	-72
58	0.34	8015	97	53.6	4.7	0.60	-48
64	0.47	7985	97	54.8	4.6	0.76	20
79	0.68	7956	96	56.5	4.5	1.34	12
93	0.94	7975	96	57.5	4.4	1.70	72
100	1.05	7974	96	56.4	4.5	1.90	100
107	1.19	8010	97	56.2	4.5	2.16	152
114	1.34	7956	96	56.2	4.5	2.39	176
124	1.57	7975	96	56.1	4.5	2.75	276

Table B.3 Freeze-thaw data for 10% MK concrete studied in series 1.

Mixture ref: ***10M 30/12***							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8349	100	53.5	4.7		0
7	-0.02	8274	98	54.2	4.6	0.00	-4
14	-0.11	8258	98	52.5	4.8	-0.02	-36
20	-0.09	8340	100	53.5	4.7	-0.03	20
30	-0.07	8283	98	52.6	4.8	0.06	-12
37	-0.02	8273	98	51.9	4.8	0.13	20
44	0.03	8107	94	52.8	4.8	0.24	-48
51	0.07	8297	99	52.4	4.8	0.37	-16
58	0.12	8322	99	52.0	4.8	0.46	32
64	0.17	8296	99	53.7	4.7	0.61	44
79	0.37	8299	99	54.0	4.6	0.90	64
93	0.50	8283	98	53.1	4.7	1.23	120
100	0.65	8396	101	53.0	4.7	1.39	56
107	0.71	8398	101	53.0	4.7	1.55	100
114	0.87	8287	99	53.1	4.7	1.73	80
124	1.10	8220	97	54.2	4.6	1.96	112

Table B.4 Freeze-thaw data for 7.5%FA-2.5%MK concrete studied in series 1.

Mixture ref: ***7.5F2.5M 20/18***							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		7982	100	54.6	4.6		0
7	-0.02	8066	102	54.5	4.6	-0.01	-40
14	-0.09	8099	103	53.4	4.7	-0.04	-28
20	-0.08	8068	102	53.1	4.7	-0.04	-28
30	-0.03	8006	101	53.6	4.7	0.07	-8
37	0.03	8125	104	53.5	4.7	0.17	-28
44	0.07	7966	100	54.2	4.6	0.33	-4
51	0.15	8150	104	55.9	4.5	0.53	20
58	0.37	8288	108	56.1	4.5	0.74	20
64	0.62	8189	105	61.8	4.1	0.94	44
79	1.02	8116	103	56.1	4.5	1.52	72
93	1.58	8144	104	56.1	4.5	2.31	52
100	1.92	8215	106	56.1	4.5	2.57	24
107	2.25	8174	105	55.4	4.5	2.78	48
114	2.51	8176	105	55.3	4.5	3.04	60
124	2.82	8172	105	55.4	4.5	3.43	76

Table B.5 Freeze-thaw data for non air-entrained control concrete.

Mixture ref: *CON 14/00*							
	Specimen *A* [α]					Specimen *B* [β]	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion ($\mu m/m$)*
0		8542	100	50.8	4.9		0
20	-0.06	7930	86	54.8	4.6	-0.04	709
30	-0.06	7599	79	57.3	4.4	-0.07	1355
40	-0.03	7056	68	60.3	4.2	-0.10	2295
50	0.06	6458	57	66.5	3.8	0.09	3088
62	0.19	5623	43	74.5	3.4	0.31	4406
74	0.53	4971	34	94.6	2.7	1.19	5518
80	0.70	3268	15	94.6	2.7	2.32	7012
91	2.19					4.32	9633
101	3.45					6.03	11378
112	4.26					8.15	12606
120	6.23					10.35	

Table B.6 Freeze-thaw data for non air-entrained concrete incorporating 2.5% MK.

Mixture ref: ***2.5M 07/00***							
	Specimen A [α]					*Specimen B* [β]	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8444	100	52.2	4.8		0
10	-0.02	8312	97	53.5	4.7	-0.03	16
15	-0.03	8294	96	52.6	4.8	-0.02	-104
21	-0.05	8338	98	52.3	4.8	-0.03	-24
28	-0.05	8370	98	52.6	4.8	-0.04	-8
38	-0.07	8296	97	53.4	4.7	-0.05	28
49	-0.03	8265	96	53.2	4.7	-0.01	72
58	-0.03	8231	95	52.8	4.8	-0.03	84
65	0.01	8238	95	53.0	4.7	-0.02	104
75	0.06	8251	95	53.2	4.7	-0.02	135
85	0.11	8142	93	54.8	4.6	0.01	219
95	0.22	8036	91	54.2	4.6	0.03	275
105	0.42	7827	86	58.4	4.3	0.09	382
110	0.56	7834	86	58.4	4.3	0.13	394
120	0.96	7536	80	61.9	4.1	0.52	534

Table B.7 Freeze-thaw data for non air-entrained concrete incorporating 7.5% MK.

Mixture ref: *7.5M 15/00*							
	Specimen *A* [α]					Specimen *B* [β]	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8391	100	51.9	4.8		0
10	-0.02	8265	97	53.4	4.7	-0.03	52
15	-0.03	8238	96	52.9	4.7	-0.02	32
21	-0.04	8289	98	53.4	4.7	-0.03	60
28	0.00	8200	95	53.3	4.7	-0.03	104
38	0.01	8083	93	52.6	4.8	-0.05	127
49	0.10	8023	91	53.8	4.7	0.09	171
58	0.15	8161	95	52.8	4.8	0.27	163
65	0.20	8134	94	52.6	4.8	0.42	191
75	0.28	8099	93	53.1	4.7	0.58	247
85	0.50	8033	92	53.4	4.7	0.91	319
95	1.06	7866	88	54.2	4.6	1.20	414
105	1.31	7867	88	55.5	4.5	1.51	490
110	1.40	7774	86	58.6	4.3	1.66	470
120	1.54	7616	82	58.2	4.3	1.81	582

Table B.8 Freeze-thaw data for non air-entrained concrete incorporating 10% MK.

Mixture ref: ***10M 30/00***							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion ($\mu m/m$)*
0		8427	100	53.2	4.7		0
10	-0.07	8179	94	54.2	4.6	-0.01	131
15	-0.04	8107	93	58.5	4.3	0.02	291
22	0.00	8017	91	57.4	4.4	0.02	426
27	0.03	7964	89	54.2	4.6	0.03	570
32	0.19	7903	88	54.0	4.6	0.12	701
37	0.24	7803	86	57.6	4.4	0.10	821
44	0.36	7514	80	60.1	4.2	0.09	1127
49	0.40	7347	76	56.1	4.5	0.21	1299
56	0.47	7270	74	56.8	4.4	0.22	1538
60	0.55	6986	69	63.7	3.9	0.29	1817
67	0.66	6977	69	59.7	4.2	0.30	2239
73	0.71	6544	60	62.2	4.0	0.42	2506
78	0.88	6134	53	64.8	3.9	0.49	2825
86	0.97	5708	46	62.8	4.0	0.56	3394
95	1.20	5102	37	67.8	3.7	0.70	4060
104	1.65	4589	30	75.5	3.3	0.86	4793
113	2.08	4073	23			1.21	5375
120	2.59	3408	16			1.62	6127

Table B.9 Freeze-thaw data for air-entrained control concrete.

Mixture ref: ***CON 18/10***							
	Specimen *A* [α]					Specimen *B* [β]	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		7906	100	54.4	4.6		0
20	0.07	7725	95	57.4	4.4	0.15	-52
30	0.21	7747	96	56.6	4.4	0.37	-44
40	0.26	7740	96	55.9	4.5	0.46	56
50	0.32	7630	93	57.1	4.4	0.56	-24
62	0.53	7656	94	57.3	4.4	0.64	4
74	0.77	7728	96	58.0	4.3	0.82	-16
80	0.97	7713	95	58.3	4.3	0.91	12
91	1.41	7695	95	57.6	4.4	1.03	12
101	1.74	7740	96	58.1	4.3	1.09	-16
112	1.98	7619	93	57.4	4.4	1.11	36
120	2.25	7652	94	57.4	4.4	1.22	-24

Table B.10 Freeze-thaw data for air-entrained concrete incorporating 2.5% MK.

Mixture ref: ***2.5M 07/06***							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss(%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8332	100	52.1	4.8		0
10	-0.01	8192	97	53.4	4.7	-0.01	32
15	-0.01	8218	97	52.7	4.8	-0.02	16
21	0.00	8210	97	52.7	4.8	0.00	-4
28	0.01	8227	97	52.7	4.8	0.00	16
38	0.02	8348	100	53.1	4.7	-0.01	12
49	0.11	8239	98	53.6	4.7	0.01	40
58	0.14	8248	98	53.0	4.7	0.08	40
65	0.20	8290	99	52.9	4.7	0.12	40
75	0.22	8275	99	52.4	4.8	0.16	40
85	0.29	8248	98	52.8	4.8	0.21	32
95	0.41	8193	97	55.6	4.5	0.32	64
105	0.52	8185	97	55.2	4.5	0.46	68
110	0.57	8284	99	55.3	4.5	0.57	60
120	0.66	8290	99	55.6	4.5	0.66	56

Table B.11 Freeze-thaw data for air-entrained concrete incorporating 7.5% MK.

Mixture ref: ***7.5M 16/10***							
	Specimen A $^{\alpha}$					*Specimen B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8168	100	53.0	4.7		0
10	-0.01	8038	97	54.4	4.6	0.03	-84
15	-0.02	8000	96	54.3	4.6	0.06	-72
21	-0.01	8040	97	54.2	4.6	0.11	-40
28	0.02	8055	97	54.3	4.6	0.14	-36
38	0.05	8185	100	54.3	4.6	0.15	-24
49	0.08	8023	96	54.1	4.6	0.17	-20
58	0.09	8031	97	53.9	4.7	0.23	-24
65	0.13	8024	97	54.1	4.6	0.28	-28
75	0.16	8020	96	53.7	4.7	0.33	12
85	0.21	8030	97	54.7	4.6	0.39	-12
95	0.30	8033	97	55.4	4.5	0.44	12
105	0.34	8093	98	55.9	4.5	0.47	4
110	0.38	8035	97	55.4	4.5	0.50	-16
120	0.42	8072	98	55.5	4.5	0.51	8

Table B.12 Freeze-thaw data for air-entrained concrete incorporating 10% MK.

Mixture ref: *10M 17/12*							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8240	100	53.8	4.7		0
10	-0.01	8232	100	54.8	4.6	-0.01	44
15	-0.02	8082	96	54.2	4.6	0.01	64
21	-0.02	8154	98	54.3	4.6	0.00	56
28	-0.03	8089	96	53.6	4.7	0.00	52
38	-0.03	8086	96	53.6	4.7	-0.04	64
49	-0.01	8155	98	53.5	4.7	-0.03	76
58	-0.01	8076	96	53.6	4.7	-0.01	100
65	-0.02	8137	98	53.6	4.7	0.02	88
75	-0.03	8097	97	53.5	4.7	0.04	88
85	0.01	8123	97	54.2	4.6	0.11	84
95	0.04	8120	97	54.1	4.6	0.16	96
105	0.04	8095	97	54.7	4.6	0.23	116
110	0.07	8115	97	54.8	4.6	0.26	84
120	0.08	8137	98	55.3	4.5	0.28	88

Table B.13 Freeze-thaw data for non air-entrained concrete incorporating 10% FA.

Mixture ref: *10F 04/00*							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8236	100	52.8	4.8		0
10	-0.37	5410	43	75.0	3.4	-0.40	2681
15	-0.69	4031	24	79.8	3.2	-0.46	3697
22	-0.40	1895	5	96.1	2.6	0.49	5036
27	-0.09					1.65	5924
32	0.21					2.09	6570
37	1.33					3.07	7351
44	4.00					5.93	8610
49	7.01					9.27	8769
56	9.77					10.67	10510
60	11.46					13.76	10789
67	20.95					23.03	

Table B.14 Freeze-thaw data for non air-entrained concrete incorporating 30% FA.

Mixture ref: ***30F 03/00***							
	Specimen *A* [α]					Specimen *B* [β]	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8120	100	53.2	4.7		0
10	-0.58	4050	25	60.6	4.1	-0.59	2458
15	0.24	1808	5	69.3	3.6	-0.67	2928
22	3.39					-0.27	4147
27	7.73					2.84	4737
32	9.49					3.93	5271
37	13.86					7.70	6076
44	15.61					12.31	7275
49	26.89					20.24	9789

Table B.15 Freeze-thaw data for air-entrained concrete incorporating 10% FA.

Mixture ref: *10F 05/24*							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		7808	100	56.3	4.5		0
20	0.08	7697	97	57.6	4.4	0.20	-28
30	0.16	7675	97	57.2	4.4	0.49	-24
40	0.19	7682	97	56.9	4.4	0.67	40
50	0.25	7695	97	57.1	4.4	0.80	-28
62	0.34	7740	98	56.9	4.4	1.02	20
74	0.40	7765	99	57.7	4.4	1.34	8
80	0.53	7763	99	57.2	4.4	1.48	48
91	0.62	7801	100	57.3	4.4	1.77	4
101	0.76	7806	100	57.0	4.4	1.92	-12
112	0.91	7803	100	56.9	4.4	2.13	40
120	1.10	7813	100	57.3	4.4	2.42	24

Table B.16 Freeze-thaw data for air-entrained concrete incorporating 30% FA.

Mixture ref: *30F 04/40*							
	Specimen A [α]					Specimen B [β]	
No. of cycles	Weight loss (%)	Resonant frequency (Hz)	Durability factor (%)	Transit time (s)	Pulse velocity (km/s)	Weight loss (%)	Expansion (μm/m)
0		7953	100	54.2	4.6		0
20	0.11	7702	94	57.7	4.4	0.23	-44
30	0.59	7754	95	56.8	4.4	0.63	-56
40	0.88	7714	94	56.4	4.5	0.98	-4
50	1.35	7715	94	57.0	4.4	1.31	-20
62	1.70	7711	94	59.6	4.2	1.64	0
74	2.20	7711	94	58.9	4.3	2.04	-28
80	2.46	7659	93	57.3	4.4	2.19	-12
91	2.91	7689	93	58.2	4.3	2.53	4
101	3.31	7512	89	59.6	4.2	2.79	12
112	3.87	7395	86	60.4	4.2	3.14	40
120	4.25	7081	79	61.7	4.1	3.36	-48

Table B.17 Freeze-thaw data for non air-entrained concrete incorporating 7.5%FA blended with 2.5%MK.

Mixture ref: *7.5F2.5M 07/00*							
	Specimen *A* $^{\alpha}$					Specimen *B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion ($\mu m/m$)*
0		8420	100	51.5	4.9		0
10	-0.10	6779	65	60.0	4.2	-0.04	398
15	-0.14	6374	57	62.3	4.0	-0.05	817
22	-0.22	5675	45	64.1	3.9	-0.16	1641
27	-0.26	5403	41	68.4	3.7	-0.16	2088
32	-0.20	5315	40	74.0	3.4	-0.10	2610
37	-0.23	4520	29	81.2	3.1	-0.06	2984
44	-0.16	3942	22	93.4	2.7	0.38	3594
49	0.55	3905	22			0.82	3960
56	1.08	3780	20			1.21	4578
60	1.57					1.59	4880
67	2.35					1.94	5518
73	4.09					3.32	5669
78	4.67					3.80	5984
86	5.48					4.72	6307
95	6.32					5.54	6873
104	8.18					6.33	7618
113	9.57					8.10	8120
120	13.53					9.76	9263

Table B.18 Freeze-thaw data for air-entrained concrete incorporating 7.5%FA blended with 2.5%MK.

Mixture ref: ***7.5F2.5M 06/18***							
	Specimen A $^{\alpha}$					*Specimen B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion ($\mu m/m$)*
0		8194	100	53.3	4.7		0
20	0.20	8092	95	55.6	4.5	0.17	-48
30	0.31	8122	97	54.6	4.6	0.28	-56
40	0.35	8071	95	53.8	4.7	0.33	-12
50	0.40	8073	95	54.7	4.6	0.41	-8
62	0.46	8121	97	54.7	4.6	0.48	-8
74	0.50	8131	97	55.2	4.6	0.58	4
80	0.58	8127	97	55.0	4.6	0.67	-24
91	0.69	8120	97	56.4	4.5	0.79	-4
101	0.77	8160	100	56.5	4.5	0.87	-20
112	0.82	8151	100	55.8	4.5	0.93	-20
120	0.90	8186	105	55.6	4.5	1.03	-36

Table B.19 Freeze-thaw data for non air-entrained concrete incorporating 22.5%FA blended with 7.5%MK.

Mixture ref: ***22.5F7.5M 04/00***							
	Specimen A $^{\alpha}$					*Specimen B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion (μm/m)*
0		8245	100	53.0	4.7		0
10	-0.50	4708	33	74.2	3.4	-0.38	1618
15	-0.78	3264	16	97.1	2.6	-0.56	2434
22	-0.24	2406	9			-0.63	3422
27	0.43					-0.53	4072
32	0.84					-0.50	4653
37	2.03					-0.38	5359
44	3.21					0.53	6100
49	3.90					1.40	6478
56	4.53					2.21	7052
60	5.48					3.44	7378
67	6.84					4.81	8761
73	8.51					5.78	9590
78	9.75					6.71	10044
86	11.87					9.08	10486
95	14.31					10.04	12124

Table B.20 Freeze-thaw data for air-entrained concrete incorporating 22.5%FA blended with 7.5%MK.

Mixture ref: *22.5F2.5M 04/40*							
	Specimen A $^{\alpha}$					*Specimen B* $^{\beta}$	
No. of cycles	*Weight loss (%)*	*Resonant frequency (Hz)*	*Durability factor (%)*	*Transit time (s)*	*Pulse velocity (km/s)*	*Weight loss (%)*	*Expansion ($\mu m/m$)*
0		7992	100	54.5	4.6		0
20	0.14	7712	93	57.6	4.4	0.15	16
30	0.25	7701	93	57.0	4.4	0.26	8
40	0.37	7772	95	56.5	4.4	0.32	40
50	0.52	7765	94	56.9	4.4	0.44	48
62	0.69	7796	95	57.8	4.3	0.64	52
74	0.91	7822	96	57.6	4.4	0.90	36
80	1.01	7800	95	57.5	4.4	0.94	56
91	1.16	7821	96	57.9	4.3	1.06	67
101	1.30	7816	96	58.1	4.3	1.26	60
112	1.46	7805	95	57.6	4.4	1.43	71
120	1.57	7823	96	58.3	4.3	1.56	8

Table B.21 Air void system parameters for non air-entrained control concrete and concretes incorporating MK.

MK content (%)	*A_{hard}* (%)	*n* (per mm)	*p* (%)	*α* (mm^{-1})	$\bar{L}$ (μm)
0	2.9	0.11	26.2	14.5	416
2.5	2.5	0.07	25.6	10.4	612
7.5	2.5	0.08	28.9	12.2	549
10	2.0	0.05	25.3	10.7	658

Table B.22 Air void system parameters for air-entrained control concrete and concretes incorporating MK.

MK content (%)	*A_{hard}* (%)	*n* (per mm)	*p* (%)	*α* (mm^{-1})	$\bar{L}$ (μm)
0	6.0	0.23	25.6	15.4	279
2.5	4.1	0.15	25.8	14.7	349
7.5	5.2	0.25	25.8	19.2	241
10	5.2	0.24	26.7	18.1	258

Table B.23 Air void system parameters for the non air-entrained control concrete and concretes incorporating FA.

Fly Ash content (%)	*A_{hard}* (%)	*n* (per mm)	*p* (%)	*α* (mm^{-1})	$\bar{L}$ (μm)
0	2.9	0.11	26.2	14.5	416
10	2.4	0.04	27.3	6.5	1037
30	1.1	0.03	28.7	10.4	922

Table B.24 Air void system parameters for the air-entrained control concrete and concretes incorporating FA.

Fly Ash content (%)	*A_{hard}* (%)	*n* (per mm)	*p* (%)	*α* (mm^{-1})	$\bar{L}$ (μm)
0	6.0	0.23	25.6	15.4	279
10	7.9	0.30	21.7	15.0	182
30	5.3	0.18	25.7	13.8	331

Table B.25 Air void system parameters for non air-entrained control concretes and concretes containing blends of FA with MK at 10 and 30% total replacement levels

Concrete	A_{hard} (%)	n (per mm)	p (%)	α (mm^{-1})	$\bar{L}$ (μm)
control	2.9	0.11	26.2	14.5	416
7.5%FA-2.5%MK	2.3	0.05	27.3	8.1	848
22.5%FA-7.5%MK	1.7	0.03	25.0	6.8	1090

Table B.26 Air void system parameters for air-entrained control concretes and concretes containing blends of FA with MK at 10 and 30% total replacement levels.

Concrete	A_{hard} (%)	n (per mm)	p (%)	α (mm^{-1})	$\bar{L}$ (μm)
control	6.0	0.23	25.6	15.4	279
7.5%FA-2.5%MK	6.4	0.27	24.8	23.1	207
22.5%FA-7.5%MK	6.2	0.21	25.1	13.7	296

Appendix C Calculation of equivalent cube strength

Part of this investigation was to examine the effect of freeze-thaw action on the compressive and flexural strength of concretes under investigation. The compressive strength at the end of freeze-thaw testing for the concretes under investigation was obtained from an equivalent cube strength test on the two portions of the 75 x 75 x 250 mm after it was tested for flexural strength. However, for these equivalent 75mm cube results to be comparable to those obtained on 100mm cubes at the beginning of the freeze-thaw testing, it was necessary to determine their equivalent 100mm cube compressive strength. In addition it was necessary to determine the flexural strength of the concretes at the beginning of the freeze-thaw testing for comparison to that obtained at the end of the testing.

Following the above problem few non air-entrained mixtures incorporating pozzolans or combinations of them, with similar w/b ratio and binder content to those prepared for specimens used for freeze-thaw testing (w/b= 0.65, b=285) were prepared and 75 x75 x 250mm prisms together with 100mmcubes were produced. The specimens were cast following the same procedures as for the specimens used for freeze-thaw testing described in section 3.4.3. After 28-days curing the cubes were tested for compressive strength and the prisms for flexural strength and equivalent cube compressive strength. The results for compressive, flexural and equivalent cube strength as given in Table C.1 were the average of three, two and four values respectively.

Figure C.1 was produced in order to establish the relationships between the concrete compressive strength obtained from the 100mm cubes and flexural strength obtained from the 75 x 75 x 250mm prisms. It would appear that there is no good correlation between these two parameters, since the correlation factor was low (R^2= 0.36). For this reason it was not possible to determine the flexural strength at the beginning of the freeze-thaw testing for the concretes under investigation in this thesis. However, as shown in Figure C.2, there is a strong relationship (R^2=0.93) between the concrete compressive strength obtained from the 100mm cubes and equivalent cube strength obtained from the 75 x 75 x 250mm prisms.

Table C.1 Compressive strength, flexural strength and equivalent cube strength results.

	100mm cubes	*75 x 75 x 250mm prisms*	
Concrete	*Compressive strength (N/mm^2)*	*Flexural strength (N/mm^2)*	*Equivalent cube strength (N/mm^2)*
Control	29.4	5.5	32.1
10%FA	38.0	7.4	42.3
30%FA	26.4	6.2	26.6
7.5%FA+2.5%MK	34.5	6.2	36.0
15%FA+5%MK	38.2	8.0	41.7
22.5%FA+7.5%MK	33.7	5.8	34.2
5%MK	33.2	6.5	34.3
7.5%MK	37.0	7.3	38.4
10%MK	41.7	7.0	45.9

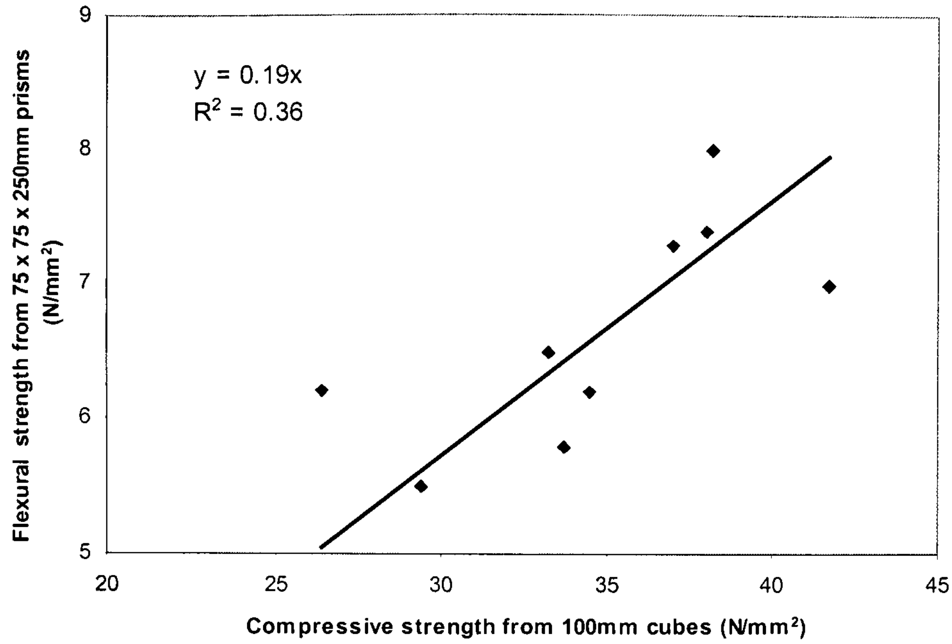

Figure C.1 Relationship between flexural strength obtained from 75 x 75 x 250 mm prisms and compressive strength obtained from 100mm cubes.

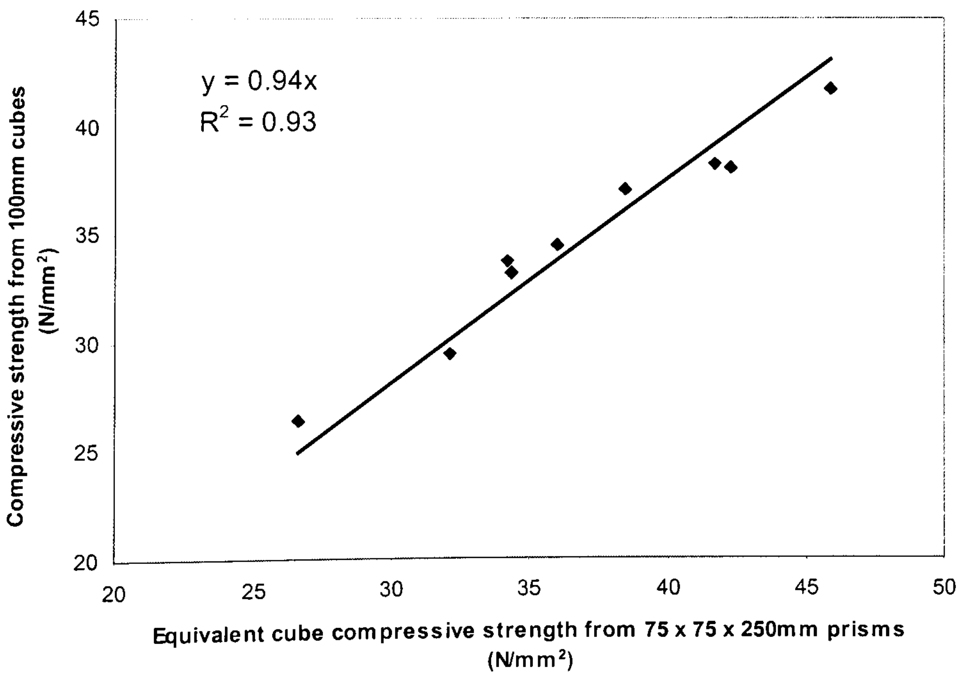

Figure C.2 Relationship between compressive strength obtained from 100 mm cubes and equivalent cube strength obtained from 75 x 75 x 250 mm prisms.

Appendix D MIP, sorptivity and water absorption data

Table D.1 MIP data for non air-entrained and air-entrained control concretes.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
Control non air-entrained	A	48.8	0.120	7.96	34.9
	B	46.1	0.120	9.97	44.3
	C	43.9	0.170	9.70	44.1
	D	30.8	0.200	9.93	44.9
	Average	42.4	0.150	9.39	42.1
Control air-entrained	A	33.5	0.850	7.34	31.8
	B	37.7	0.290		54.3
	C	40.7	0.520	14.48	70.6
	D	41.3	0.280	8.04	36.6
	Average	38.3	0.490	9.95	48.3

Table D.2 MIP data for non air-entrained and air-entrained concretes incorporating 2.5% MK.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
2.5% MK non air-entrained	A	48.2	0.120	19.69	100.0
	B	45.4	0.088	11.05	46.5
	C	52.5	0.120	19.40	114.8
	D	67.5	0.100		158.9
	Average	53.4	0.110	16.71	105.1
2.5% MK air-entrained	A	40.7	0.120	15.66	66.9
	B	53.8	0.140		43.2
	C	37.7	0.400	22.62	112.0
	D	45.4	0.180	28.58	106.3
	Average	44.4	0.210	22.29	82.1

Table D.3 MIP data for non air-entrained and air-entrained concretes incorporating 7.5% MK.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
7.5% MK non air-entrained	A	76.5	0.052	18.29	83.5
	B	82.5	0.058	13.80	46.3
	C	70.1	0.067	16.94	80.3
	D	71.8	0.051		17.9
	Average	75.2	0.060	16.34	57.0
7.5% MK air-entrained	A	64.0	0.061	21.34	109.5
	B	41.8	0.070		54.0
	C	58.5	0.082	22.13	112.9
	D	51.6	0.062	16.20	56.5
	Average	54.0	0.070	19.89	83.2

Table D.4 MIP data for non air-entrained and air-entrained concretes incorporating 10% MK.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
10% MK non air-entrained	A	77.1	0.062	13.36	64.6
	B	76.3	0.057	12.03	66.5
	C	83.2	0.059	16.68	94.3
	D	70.6	0.053		46.2
	Average	76.8	0.060	14.02	67.9
10% MK air-entrained	A	51.0	0.053	20.4	104.7
	B	59.0	0.049	14.25	46.9
	C	55.3	0.052	22.95	112.0
	D	56.2	0.047		36.3
	Average	55.4	0.050	19.20	75.0

Table D.5 MIP data for non air-entrained and air-entrained concretes incorporating 10% FA.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
10% FA non air-entrained	A	41.7	0.390		69.4
	B	40.3	0.180	15.62	89.3
	C	44.5	0.260	14.60	88.5
	D	40.9	0.190	20.04	117.9
	Average	41.8	0.260	16.75	91.3
10% FA air-entrained	A	40.6	0.350	17.82	95.9
	B	36.3	0.330	11.33	57.9
	C	33.6	0.300		40.0
	D	30.4	0.550	16.06	89.7
	Average	35.2	0.380	15.07	70.9

Table D.6 MIP data for non air-entrained and air-entrained concretes incorporating 30% FA.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
30% FA non air-entrained	A	45.9	0.180		71.7
	B	47.5	0.190	19.05	109.5
	C	45.7	0.190	18.29	104.0
	D	49.5	0.150	18.97	111.0
	Average	47.1	0.180	18.77	99.0
30% FA air-entrained	A	39.3	0.400	15.28	77.6
	B	37.0	0.490	22.55	133.5
	C	40.4	0.380	21.17	119.0
	D	29.9	0.550	13.86	70.4
	Average	36.7	0.460	18.22	100.1

Table D.7 MIP data for non air-entrained and air-entrained concretes incorporating a blend of 7.5% FA and 2.5% MK.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
7.5%FA-2.5% MK non air-entrained	A	53.6	0.120	15.29	85.0
	B	50.7	0.120	17.40	94.6
	C	60.3	0.110	17.53	106.9
	D	52.7	0.100	16.01	83.9
	Average	54.3	0.110	16.56	92.6
7.5%FA-2.5% MK air-entrained	A	44.4	0.270	14.73	79.2
	B	48.3	0.100	15.70	49.9
	C	45.7	0.180	10.42	76.3
	D				
	Average	46.1	0.180	13.62	68.5

Table D.8 MIP data for non air-entrained and air-entrained concretes incorporating a blend of 22.5% FA and 7.5% MK.

Concrete	Sample	% pores< 0.05 μm radius	Threshold radius (μm)	Total porosity (%)	Intruded pore volume (mm^3/g)
22.5%FA-7.5% MK non air-entrained	A	71.0	0.065	19.94	113.3
	B	69.2	0.060	16.92	103.9
	C	60.1	0.092	18.77	111.1
	D	66.4	0.078	17.65	110.4
	Average	66.7	0.070	18.32	109.7
22.5%FA-7.5% MK air-entrained	A	60.1	0.061		38.1
	B	57.0	0.092	18.03	93.9
	C	59.5	0.069	16.62	73.2
	D	59.0	0.069	15.98	85.5
	Average	58.9	0.070	16.88	72.7

Table D.9 Sorptivity and water absorption data for non air-entrained and air-entrained control concretes.

Concrete	*Sample*	*Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Water absorption (%)*
control non air-entrained	A	2.31	2.9	4.5
	B	2.32	2.67	4.5
	Average		2.79	4.5
control air-entrained	A	2.15	2.58	4.4
	B	1.73	2.45	4.4
	Average		2.52	4.4

Table D.10 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating 2.5% MK.

Concrete	*Sample*	*Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Water absorption (%)*
2.5% MK non air-entrained	A	2.66	2.74	4.3
	B	2.53	2.68	4.1
	Average		2.71	4.2
2.5% MK air-entrained	A	2.49	2.46	4.7
	B	2.34	2.31	4.7
	Average		2.38	4.7

Table D.11 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating 7.5% MK.

Concrete	*Sample*	*Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Water absorption (%)*
7.5% MK non air-entrained	A	1.99	2.65	4.8
	B	2.11	2.68	4.6
	Average		2.67	4.7
7.5% MK air-entrained	A	1.88	2.24	4.8
	B	2.00	2.38	4.6
	Average		2.31	4.7

Table D.12 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating 10% MK.

Concrete	Sample	Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)	Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)	Water absorption (%)
10% MK non air-entrained	A	1.63	1.92	4.8
	B	1.50	1.81	4.9
	Average		1.87	4.8
10% MK air-entrained	A	1.51	1.96	4.9
	B	1.79	2.03	4.9
	Average		2.00	4.9

Table D.13 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating 10% FA.

Concrete	Sample	Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)	Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)	Water absorption (%)
10% FA non air-entrained	A	2.00	2.76	4.6
	B	2.17	2.66	4.7
	Average		2.71	4.6
10% FA air-entrained	A	2.18	2.47	4.8
	B	1.91	2.27	4.8
	Average		2.37	4.8

Table D.14 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating 30% FA.

Concrete	Sample	Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)	Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)	Water absorption (%)
30% FA non air-entrained	A	1.91	2.19	4.9
	B	1.91	2.06	4.8
	Average		2.13	4.8
30% FA air-entrained	A	2.24	2.54	5.5
	B	2.01	2.42	5.4
	Average		2.48	5.4

Table D.15 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating a blend of 7.5% FA and 2.5% MK.

Concrete	*Sample*	*Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Water absorption (%)*
7.5%FA-2.5% MK non air-entrained	A	2.06	2.43	4.8
	B	1.59	1.76	4.7
	Average		2.10	4.7
7.5%FA-2.5% MK air-entrained	A	1.75	2.19	4.9
	B	1.78	2.23	4.7
	Average		2.21	4.8

Table D.16 Sorptivity and water absorption data for non air-entrained and air-entrained concretes incorporating a blend of 22.5% FA and 7.5% MK.

Concrete	*Sample*	*Sorptivity 0-4 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Sorptivity 4-8 $min^{0.5}$ ($g/mm^2min^{0.5}$)*	*Water absorption (%)*
22.5%FA-7.5% MK non air-entrained	A	1.70	1.89	5.1
	B	1.93	2.09	5.1
	Average		1.99	5.1
22.5%FA-7.5% MK air-entrained	A	1.36	1.76	5.2
	B	1.27	1.57	5.3
	Average		1.67	5.3

Appendix E Publications

Chistodoulou, G, 2000. A comparative study of the effects of silica fume, metakaolin and PFA on the air content of fresh concrete. SCI LECTURE PAPERS SERIES, ISSN 1353-114X, LPS 109/2000,http://sci.mond.org/lecturepapers/papers/lps109.pdf

Award winning paper for the best presentation at the Young Researchers Forum, organised by the SCI Construction Materials Group, held 27 April 2000, SCI London, UK